



US009425217B2

(12) **United States Patent**
Ishihara et al.

(10) **Patent No.:** **US 9,425,217 B2**
(45) **Date of Patent:** **Aug. 23, 2016**

(54) **SEMICONDUCTOR DEVICE**

USPC 257/43
See application file for complete search history.

(71) Applicant: **Semiconductor Energy Laboratory Co., Ltd.**, Atsugi-shi, Kanagawa-ken (JP)

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,731,856 A 3/1998 Kim et al.
5,744,864 A 4/1998 Cillessen et al.

(Continued)

FOREIGN PATENT DOCUMENTS

EP 1737044 A 12/2006
EP 2226847 A 9/2010

(Continued)

OTHER PUBLICATIONS

Coates.D et al., "Optical Studies of the Amorphous Liquid-Cholesteric Liquid Crystal Transition: The "Blue Phase"", Physics Letters, Sep. 10, 1973, vol. 45A, No. 2, pp. 115-116.

(Continued)

(72) Inventors: **Noritaka Ishihara**, Koza (JP); **Masashi Oota**, Atsugi (JP); **Masashi Tsubuku**, Atsugi (JP); **Masami Jintyou**, Shimotsuga (JP); **Yukinori Shima**, Tatebayashi (JP); **Junichi Koezuka**, Tochigi (JP); **Yasuharu Hosaka**, Tochigi (JP); **Shunpei Yamazaki**, Setagaya (JP)

(73) Assignee: **Semiconductor Energy Laboratory Co., Ltd.**, Kanagawa-ken (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/486,089**

(22) Filed: **Sep. 15, 2014**

(65) **Prior Publication Data**

US 2015/0084043 A1 Mar. 26, 2015

(30) **Foreign Application Priority Data**

Sep. 23, 2013 (JP) 2013-196333

(51) **Int. Cl.**
H01L 29/10 (2006.01)
H01L 27/12 (2006.01)

(Continued)

(52) **U.S. Cl.**
CPC **H01L 27/1225** (2013.01); **H01L 29/41733** (2013.01); **H01L 29/45** (2013.01);
(Continued)

(58) **Field of Classification Search**

CPC H01L 27/1225; H01L 29/45; H01L 29/41733; H01L 29/7869; H01L 29/78696

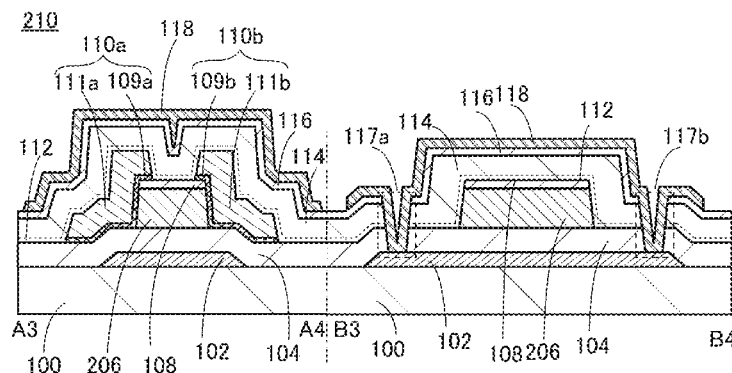
Primary Examiner — Elias M Ullah

(74) *Attorney, Agent, or Firm* — Robinson Intellectual Property Law Office; Eric J. Robinson

(57) **ABSTRACT**

Defects in an oxide semiconductor film are reduced in a semiconductor device including the oxide semiconductor film. The electrical characteristics of a semiconductor device including an oxide semiconductor film are improved. The reliability of a semiconductor device including an oxide semiconductor film is improved. A semiconductor device including an oxide semiconductor layer; a metal oxide layer in contact with the oxide semiconductor layer, the metal oxide layer including an In-M oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf); and a conductive layer in contact with the metal oxide layer, the conductive layer including copper, aluminum, gold, or silver is provided. In the semiconductor device, $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where the atomic ratio of In to M included in the metal oxide layer is In:M=x:y.

20 Claims, 29 Drawing Sheets



- (51) **Int. Cl.**
H01L 29/45 (2006.01)
H01L 29/417 (2006.01)
H01L 29/786 (2006.01)
- (52) **U.S. Cl.**
CPC **H01L29/7869** (2013.01); **H01L 29/78648**
(2013.01); **H01L 29/78693** (2013.01); **H01L**
29/78696 (2013.01)
- (56) **References Cited**
U.S. PATENT DOCUMENTS
- | | | | |
|--------------|-----|---------|---------------------------------------|
| 6,294,274 | B1 | 9/2001 | Kawazoe et al. |
| 6,563,174 | B2 | 5/2003 | Kawasaki et al. |
| 6,727,522 | B1 | 4/2004 | Kawasaki et al. |
| 7,049,190 | B2 | 5/2006 | Takeda et al. |
| 7,061,014 | B2 | 6/2006 | Hosono et al. |
| 7,064,346 | B2 | 6/2006 | Kawasaki et al. |
| 7,105,868 | B2 | 9/2006 | Nause et al. |
| 7,211,825 | B2 | 5/2007 | Shih et al. |
| 7,282,782 | B2 | 10/2007 | Hoffman et al. |
| 7,297,977 | B2 | 11/2007 | Hoffman et al. |
| 7,323,356 | B2 | 1/2008 | Hosono et al. |
| 7,385,224 | B2 | 6/2008 | Ishii et al. |
| 7,402,506 | B2 | 7/2008 | Levy et al. |
| 7,411,209 | B2 | 8/2008 | Endo et al. |
| 7,453,065 | B2 | 11/2008 | Saito et al. |
| 7,453,087 | B2 | 11/2008 | Iwasaki |
| 7,462,862 | B2 | 12/2008 | Hoffman et al. |
| 7,468,304 | B2 | 12/2008 | Kaji et al. |
| 7,501,293 | B2 | 3/2009 | Ito et al. |
| 7,652,740 | B2 | 1/2010 | Hwang et al. |
| 7,674,650 | B2 | 3/2010 | Akimoto et al. |
| 7,732,819 | B2 | 6/2010 | Akimoto et al. |
| 7,994,500 | B2 | 8/2011 | Kim et al. |
| 8,148,779 | B2 | 4/2012 | Jeong et al. |
| 8,188,480 | B2 | 5/2012 | Itai |
| 8,203,143 | B2 | 6/2012 | Imai |
| 8,471,256 | B2 | 6/2013 | Yamazaki et al. |
| 8,816,349 | B2 | 8/2014 | Yamazaki et al. |
| 2001/0046027 | A1 | 11/2001 | Tai et al. |
| 2002/0056838 | A1 | 5/2002 | Ogawa |
| 2002/0132454 | A1 | 9/2002 | Ohtsu et al. |
| 2003/0189401 | A1 | 10/2003 | Kido et al. |
| 2003/0218222 | A1 | 11/2003 | Wager et al. |
| 2004/0038446 | A1 | 2/2004 | Takeda et al. |
| 2004/0127038 | A1 | 7/2004 | Carcia et al. |
| 2005/0017302 | A1 | 1/2005 | Hoffman |
| 2005/0199959 | A1 | 9/2005 | Chiang et al. |
| 2006/0035452 | A1 | 2/2006 | Carcia et al. |
| 2006/0043377 | A1 | 3/2006 | Hoffman et al. |
| 2006/0091793 | A1 | 5/2006 | Baude et al. |
| 2006/0108529 | A1 | 5/2006 | Saito et al. |
| 2006/0108636 | A1 | 5/2006 | Sano et al. |
| 2006/0110867 | A1 | 5/2006 | Yabuta et al. |
| 2006/0113536 | A1 | 6/2006 | Kumomi et al. |
| 2006/0113539 | A1 | 6/2006 | Sano et al. |
| 2006/0113549 | A1 | 6/2006 | Den et al. |
| 2006/0113565 | A1 | 6/2006 | Abe et al. |
| 2006/0169973 | A1 | 8/2006 | Isa et al. |
| 2006/0170111 | A1 | 8/2006 | Isa et al. |
| 2006/0197092 | A1 | 9/2006 | Hoffman et al. |
| 2006/0208977 | A1 | 9/2006 | Kimura |
| 2006/0228974 | A1 | 10/2006 | Thelss et al. |
| 2006/0231882 | A1 | 10/2006 | Kim et al. |
| 2006/0238135 | A1 | 10/2006 | Kimura |
| 2006/0244107 | A1 | 11/2006 | Sugihara et al. |
| 2006/0284171 | A1 | 12/2006 | Levy et al. |
| 2006/0284172 | A1 | 12/2006 | Ishii |
| 2006/0292777 | A1 | 12/2006 | Dunbar |
| 2007/0024187 | A1 | 2/2007 | Shin et al. |
| 2007/0046191 | A1 | 3/2007 | Saito |
| 2007/0052025 | A1 | 3/2007 | Yabuta |
| 2007/0054507 | A1 | 3/2007 | Kaji et al. |
| 2007/0090365 | A1 | 4/2007 | Hayashi et al. |
| 2007/0108446 | A1 | 5/2007 | Akimoto |
| 2007/0152217 | A1 | 7/2007 | Lai et al. |
| 2007/0172591 | A1 | 7/2007 | Seo et al. |
| 2007/0187678 | A1 | 8/2007 | Hirao et al. |
| 2007/0187760 | A1 | 8/2007 | Furuta et al. |
| 2007/0194379 | A1 | 8/2007 | Hosono et al. |
| 2007/0252928 | A1 | 11/2007 | Ito et al. |
| 2007/0272922 | A1 | 11/2007 | Kim et al. |
| 2007/0287296 | A1 | 12/2007 | Chang |
| 2008/0006877 | A1 | 1/2008 | Mardilovich et al. |
| 2008/0038882 | A1 | 2/2008 | Takechi et al. |
| 2008/0038929 | A1 | 2/2008 | Chang |
| 2008/0050595 | A1 | 2/2008 | Nakagawara et al. |
| 2008/0073653 | A1 | 3/2008 | Iwasaki |
| 2008/0083950 | A1 | 4/2008 | Pan et al. |
| 2008/0106191 | A1 | 5/2008 | Kawase |
| 2008/0128689 | A1 | 6/2008 | Lee et al. |
| 2008/0129195 | A1 | 6/2008 | Ishizaki et al. |
| 2008/0166834 | A1 | 7/2008 | Kim et al. |
| 2008/0182358 | A1 | 7/2008 | Cowdery-Corvan et al. |
| 2008/0224133 | A1 | 9/2008 | Park et al. |
| 2008/0254569 | A1 | 10/2008 | Hoffman et al. |
| 2008/0258139 | A1 | 10/2008 | Ito et al. |
| 2008/0258140 | A1 | 10/2008 | Lee et al. |
| 2008/0258141 | A1 | 10/2008 | Park et al. |
| 2008/0258143 | A1 | 10/2008 | Kim et al. |
| 2008/0296568 | A1 | 12/2008 | Ryu et al. |
| 2009/0068773 | A1 | 3/2009 | Lai et al. |
| 2009/0073325 | A1 | 3/2009 | Kuwabara et al. |
| 2009/0114910 | A1 | 5/2009 | Chang |
| 2009/0134399 | A1 | 5/2009 | Sakakura et al. |
| 2009/0152506 | A1 | 6/2009 | Umeda et al. |
| 2009/0152541 | A1 | 6/2009 | Maekawa et al. |
| 2009/0278122 | A1 | 11/2009 | Hosono et al. |
| 2009/0280600 | A1 | 11/2009 | Hosono et al. |
| 2010/0065844 | A1 | 3/2010 | Tokunaga |
| 2010/0092800 | A1 | 4/2010 | Itagaki et al. |
| 2010/0109002 | A1 | 5/2010 | Itagaki et al. |
| 2011/0193083 | A1 | 8/2011 | Kim et al. |
| 2013/0207111 | A1 | 8/2013 | Yamazaki |
| 2013/0320334 | A1* | 12/2013 | Yamazaki H01L 29/7869
257/43 |
| 2014/0021466 | A1 | 1/2014 | Yamazaki et al. |
| 2014/0306221 | A1 | 10/2014 | Yamazaki et al. |
- FOREIGN PATENT DOCUMENTS
- | | | | |
|----|----------------|---|---------|
| JP | 60-198861 | A | 10/1985 |
| JP | 63-210022 | A | 8/1988 |
| JP | 63-210023 | A | 8/1988 |
| JP | 63-210024 | A | 8/1988 |
| JP | 63-215519 | A | 9/1988 |
| JP | 63-239117 | A | 10/1988 |
| JP | 63-265818 | A | 11/1988 |
| JP | 05-251705 | A | 9/1993 |
| JP | 08-264794 | A | 10/1996 |
| JP | 11-505377 | | 5/1999 |
| JP | 2000-044236 | A | 2/2000 |
| JP | 2000-150900 | A | 5/2000 |
| JP | 2002-076356 | A | 3/2002 |
| JP | 2002-289859 | A | 10/2002 |
| JP | 2003-086000 | A | 3/2003 |
| JP | 2003-086808 | A | 3/2003 |
| JP | 2004-103957 | A | 4/2004 |
| JP | 2004-133422 | A | 4/2004 |
| JP | 2004-273614 | A | 9/2004 |
| JP | 2004-273732 | A | 9/2004 |
| JP | 2007-096055 | A | 4/2007 |
| WO | WO-2004/114391 | | 12/2004 |
- OTHER PUBLICATIONS
- Meiboom.S et al., "Theory of the Blue Phase of Cholesteric Liquid Crystals", Phys. Rev. Lett. (Physical Review Letters), May 4, 1981, vol. 46, No. 18, pp. 1216-1219.
- Costello.M et al., "Electron Microscopy of a Cholesteric Liquid Crystal and Its Blue Phase", Phys. Rev. A (Physical Review. A), May 1, 1984, vol. 29, No. 5, pp. 2957-2959.

(56)

References Cited

OTHER PUBLICATIONS

- Kimizuka.N et al., "Spinel, YbFe₂O₄, and Yb₂Fe₃O₇ Types of Structures for Compounds in the In₂O₃—Ga₂ZnO₄—BO Systems [A: Fe, Ga, or Al; B: Mg, Mn, Fe, Ni, Cu, or Zn] at Temperatures Over 1000° C.", *Journal of Solid State Chemistry*, 1985, vol. 60, pp. 382-384.
- Nakamura.M et al., "The phase relations in the In₂O₃—Ga₂ZnO₄—ZnO system at 1350° C.", *Journal of Solid State Chemistry*, Aug. 1, 1991, vol. 93, No. 2, pp. 298-315.
- Kitzerow.H et al., "Observation of Blue Phases in Chiral Networks", *Liquid Crystals*, 1993, vol. 14, No. 3, pp. 911-916.
- Kimizuka.N et al., "Syntheses and Single-Crystal Data of Homologous Compounds, In₂O₃(ZnO)_m (m=3, 4, and 5), InGaO₃(ZnO)₃, and Ga₂O₃(ZnO)_m (m=7, 8, 9, and 16) in the In₂O₃—ZnGa₂O₄—ZnO System", *Journal of Solid State Chemistry*, Apr. 1, 1995, vol. 116, No. 1, pp. 170-178.
- Chern.H et al., "An Analytical Model for the Above-Threshold Characteristics of Polysilicon Thin-Film Transistors", *IEEE Transactions on Electron Devices*, Jul. 1, 1995, vol. 42, No. 7, pp. 1240-1246.
- Prins.M et al., "A Ferroelectric Transparent Thin-Film Transistor", *Appl. Phys. Lett. (Applied Physics Letters)*, Jun. 17, 1996, vol. 68, No. 25, pp. 3650-3652.
- Li.C et al., "Modulated Structures of Homologous Compounds InMO₃(ZnO)_m (M=In,Ga; m=Integer) Described by Four-Dimensional Superspace Group", *Journal of Solid State Chemistry*, 1998, vol. 139, pp. 347-355.
- Kikuchi.H et al., "Polymer-Stabilized Liquid Crystal Blue Phases", *Nature Materials*, Sep. 2, 2002, vol. 1, pp. 64-68.
- Tsuda.K et al., "Ultra Low Power Consumption Technologies for Mobile TFT-LCDs", *IDW '02: Proceedings of the 9th International Display Workshops*, Dec. 4, 2002, pp. 295-298.
- Nomura.K et al., "Thin-Film Transistor Fabricated in Single-Crystalline Transparent Oxide Semiconductor", *Science*, May 23, 2003, vol. 300, No. 5623, pp. 1269-1272.
- Ikeda.T et al., "Full-Functional System Liquid Crystal Display Using CG-Silicon Technology", *SID Digest '04: SID International Symposium Digest of Technical Papers*, 2004, vol. 35, pp. 860-863.
- Nomura.K et al., "Room-Temperature Fabrication of Transparent Flexible Thin-Film Transistors Using Amorphous Oxide Semiconductors", *Nature*, Nov. 25, 2004, vol. 432, pp. 488-492.
- Dembo.H et al., "RFCPUS on Glass and Plastic Substrates Fabricated by TFT Transfer Technology", *IEDM 05: Technical Digest of International Electron Devices Meeting*, Dec. 5, 2005, pp. 1067-1069.
- Kanno.H et al., "White Stacked Electrophosphorescent Organic Light-Emitting Devices Employing MoO₃ as a Charge-Generation Layer", *Adv. Mater. (Advanced Materials)*, 2006, vol. 18, No. 3, pp. 339-342.
- Lee.H et al., "Current Status of, Challenges to, and Perspective View of AM-OLED", *IDW '06: Proceedings of the 13th International Display Workshops*, Dec. 7, 2006, pp. 663-666.
- Hosono.H, "68.3:Invited Paper:Transparent Amorphous Oxide Semiconductors for High Performance TFT", *SID Digest '07: SID International Symposium Digest of Technical Papers*, 2007, vol. 38, pp. 1830-1833.
- Hirao.T et al., "Novel Top-Gate Zinc Oxide Thin-Film Transistors (ZnO TFTs) for AMLCDs", *Journal of the SID*, 2007, vol. 15, No. 1, pp. 17-22.
- Park.S et al., "Challenge to Future Displays: Transparent AM-OLED Driven by PEALD Grown ZnO TFT", *IMID '07 Digest*, 2007, pp. 1249-1252.
- Kikuchi.H et al., "62.2:Invited Paper:Fast Electro-Optical Switching in Polymer-Stabilized Liquid Crystalline Blue Phases for Display Application", *SID Digest '07: SID International Symposium Digest of Technical Papers*, 2007, vol. 38, pp. 1737-1740.
- Miyasaka.M, "SUTFLA Flexible Microelectronics on Their Way to Business", *SID Digest '07: SID International Symposium Digest of Technical Papers*, 2007, vol. 38, pp. 1673-1676.
- Kurokawa.Y et al., "UHF RFCPUS on Flexible and Glass Substrates for Secure RFID Systems", *Journal of Solid-State Circuits*, 2008, vol. 43, No. 1, pp. 292-299.
- Jeong.J et al., "3.1: Distinguished Paper: 12.1-Inch WXGA AMOLED Display Driven by Indium—Gallium—Zinc Oxide TFTs Array", *SID Digest '08: SID International Symposium Digest of Technical Papers*, May 20, 2008, vol. 39, No. 1, pp. 1-4.
- Lee.J et al., "World's Largest (15-Inch) XGA AMLCD Panel Using IGZO Oxide TFT", *SID Digest '08: SID International Symposium Digest of Technical Papers*, May 20, 2008, vol. 39, pp. 625-628.
- Park.J et al., "Amorphous Indium—Gallium—Zinc Oxide TFTs and Their Application for Large Size AMOLED", *AM-FPD '08 Digest of Technical Papers*, Jul. 2, 2008, pp. 275-278.
- Takahashi.M et al., "Theoretical Analysis of IGZO Transparent Amorphous Oxide Semiconductor", *IDW '08: Proceedings of the 15th International Display Workshops*, Dec. 3, 2008, pp. 1637-1640.
- Sakata.J et al., "Development of 4.0-In. AMOLED Display With Driver Circuit Using Amorphous In—Ga—Zn—Oxide TFTs", *IDW '09: Proceedings of the 16th International Display Workshops*, 2009, pp. 689-692.
- Asaoka.Y et al., "29.1: Polarizer-Free Reflective LCD Combined With Ultra Low-Power Driving Technology", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 395-398.
- Nowatari.H et al., "60.2: Intermediate Connector With Suppressed Voltage Loss for White Tandem OLEDs", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, vol. 40, pp. 899-902.
- Jin.D et al., "65.2:Distinguished Paper:World-Largest (6.5") Flexible Full Color Top Emission AMOLED Display on Plastic Film and Its Bending Properties", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 983-985.
- Lee.M et al., "15.4:Excellent Performance of Indium—Oxide-Based Thin-Film Transistors by DC Sputtering", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 191-193.
- Cho.D et al., "21.2:Al and Sn-Doped Zinc Indium Oxide Thin Film Transistors for AMOLED Back-Plane", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 280-283.
- Kikuchi.H et al., "39.1:Invited Paper:Optically Isotropic Nano-Structured Liquid Crystal Composites for Display Applications", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 578-581.
- Osada.T et al., "15.2: Development of Driver-Integrated Panel using Amorphous In—Ga—Zn—Oxide TFT", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 184-187.
- Ohara.H et al., "21.3:4.0 In. QVGA AMOLED Display Using In—Ga—Zn—Oxide TFTs With a Novel Passivation Layer", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 284-287.
- Godo.H et al., "P-9:Numerical Analysis on Temperature Dependence of Characteristics of Amorphous In—Ga—Zn—Oxide TFT", *SID Digest '09: SID International Symposium Digest of Technical Papers*, May 31, 2009, pp. 1110-1112.
- Osada.T et al., "Development of Driver-Integrated Panel Using Amorphous In—Ga—Zn—Oxide TFT", *AM-FPD '09 Digest of Technical Papers*, Jul. 1, 2009, pp. 33-36.
- Godo.H et al., "Temperature Dependence of Characteristics and Electronic Structure for Amorphous In—Ga—Zn—Oxide TFT", *AM-FPD '09 Digest of Technical Papers*, Jul. 1, 2009, pp. 41-44.
- Ohara.H et al., "Amorphous In—Ga—Zn—Oxide TFTs with Suppressed Variation for 4.0 inch QVGA AMOLED Display", *AM-FPD '09 Digest of Technical Papers*, Jul. 1, 2009, pp. 227-230, The Japan Society of Applied Physics.
- Park.J et al., "High performance amorphous oxide thin film transistors with self-aligned top-gate structure", *IEDM 09: Technical Digest of International Electron Devices Meeting*, Dec. 7, 2009, pp. 191-194.
- Nakamura.M, "Synthesis of Homologous Compound with New Long-Period Structure", *NIRIM Newsletter*, Mar. 1, 1995, vol. 150, pp. 1-4.

(56)

References Cited

OTHER PUBLICATIONS

- Hosono.H et al., "Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and examples", J. Non-Cryst. Solids (Journal of Non-Crystalline Solids), 1996, vol. 198-200, pp. 165-169.
- Orita.M et al., "Mechanism of Electrical Conductivity of Transparent InGaZnO₄", Phys. Rev. B (Physical Review. B), Jan. 15, 2000, vol. 61, No. 3, pp. 1811-1816.
- Van de Walle.C, "Hydrogen as a Cause of Doping in Zinc Oxide", Phys. Rev. Lett. (Physical Review Letters), Jul. 31, 2000, vol. 85, No. 5, pp. 1012-1015.
- Orita.M et al., "Amorphous transparent conductive oxide InGaO₃(ZnO)_m (m<4): a Zn₄s conductor", Philosophical Magazine, 2001, vol. 81, No. 5, pp. 501-515.
- Janotti.A et al., "Oxygen Vacancies in ZnO", Appl. Phys. Lett. (Applied Physics Letters), 2005, vol. 87, pp. 122102-1-122102-3.
- Clark.S et al., "First Principles Methods Using CASTEP", Zeitschrift für Kristallographie, 2005, vol. 220, pp. 567-570.
- Nomura.K et al., "Amorphous Oxide Semiconductors for High-Performance Flexible Thin-Film Transistors", Jpn. J. Appl. Phys. (Japanese Journal of Applied Physics), 2006, vol. 45, No. 5B, pp. 4303-4308.
- Janotti.A et al., "Native Point Defects in ZnO", Phys. Rev. B (Physical Review. B), Oct. 4, 2007, vol. 76, No. 16, pp. 165202-1-165202-22.
- Lany.S et al., "Dopability, Intrinsic Conductivity, and Nonstoichiometry of Transparent Conducting Oxides", Phys. Rev. Lett. (Physical Review Letters), Jan. 26, 2007, vol. 98, pp. 045501-1-045501-4.
- Park.J et al., "Improvements in the Device Characteristics of Amorphous Indium Gallium Zinc Oxide Thin-Film Transistors by Ar Plasma Treatment", Appl. Phys. Lett. (Applied Physics Letters), Jun. 26, 2007, vol. 90, No. 26, pp. 262106-1-262106-3.
- Park.J et al., "Electronic Transport Properties of Amorphous Indium—Gallium—Zinc Oxide Semiconductor Upon Exposure to Water", Appl. Phys. Lett. (Applied Physics Letters), 2008, vol. 92, pp. 072104-1-072104-3.
- Hsieh.H et al., "P-29: Modeling of Amorphous Oxide Semiconductor Thin Film Transistors and Subgap Density of States", SID Digest '08: SID International Symposium Digest of Technical Papers, May 20, 2008, vol. 39, pp. 1277-1280.
- Oba.F et al., "Defect energetics in ZnO: A hybrid Hartree-Fock density functional study", Phys. Rev. B (Physical Review. B), 2008, vol. 77, pp. 245202-1-245202-6.
- Kim.S et al., "High-Performance oxide thin film transistors passivated by various gas plasmas", 214th ECS Meeting, 2008, No. 2317, ECS.
- Hayashi.R et al., "42.1: Invited Paper: Improved Amorphous In—Ga—Zn—O TFTs", SID Digest '08: SID International Symposium Digest of Technical Papers, May 20, 2008, vol. 39, pp. 621-624.
- Son.K et al., "42.4L: Late-News Paper: 4 Inch QVGA AMOLED Driven by the Threshold Voltage Controlled Amorphous GIZO (Ga₂O₃—In₂O₃—ZnO) TFT", SID Digest '08: SID International Symposium Digest of Technical Papers, May 20, 2008, vol. 39, pp. 633-636.
- Park.Sang-Hee et al., "42.3: Transparent ZnO Thin Film Transistor for the Application of High Aperture Ratio Bottom Emission AM-OLED Display", SID Digest '08: SID International Symposium Digest of Technical Papers, May 20, 2008, vol. 39, pp. 629-632.
- Fung.T et al., "2-D Numerical Simulation of High Performance Amorphous In—Ga—Zn—O TFTs for Flat Panel Displays", AM-FPD '08 Digest of Technical Papers, Jul. 2, 2008, pp. 251-252, The Japan Society of Applied Physics.
- Mo.Y et al., "Amorphous Oxide TFT Backplanes for Large Size AMOLED Displays", IDW '08: Proceedings of the 6th International Display Workshops, Dec. 3, 2008, pp. 581-584.
- Asakuma.N et al., "Crystallization and Reduction of Sol-Gel-Derived Zinc Oxide Films by Irradiation With Ultraviolet Lamp", Journal of Sol-Gel Science and Technology, 2003, vol. 26, pp. 181-184.
- Fortunato.E et al., "Wide-Bandgap High-Mobility ZnO Thin-Film Transistors Produced at Room Temperature", Appl. Phys. Lett. (Applied Physics Letters), Sep. 27, 2004, vol. 85, No. 13, pp. 2541-2543.
- Masuda.S et al., "Transparent thin film transistors using ZnO as an active channel layer and their electrical properties", J. Appl. Phys. (Journal of Applied Physics), Feb. 1, 2003, vol. 93, No. 3, pp. 1624-1630.
- Oh.M et al., "Improving the Gate Stability of ZnO Thin-Film Transistors With Aluminum Oxide Dielectric Layers", J. Electrochem. Soc. (Journal of the Electrochemical Society), 2008, vol. 155, No. 12, pp. H1009-H1014.
- Park.J et al., "Dry etching of ZnO films and plasma-induced damage to optical properties", J. Vac. Sci. Technol. B (Journal of Vacuum Science & Technology B), Mar. 1, 2003, vol. 21, No. 2, pp. 800-803.
- Ueno.K et al., "Field-Effect Transistor on SrTiO₃ With Sputtered Al₂O₃ Gate Insulator", Appl. Phys. Lett. (Applied Physics Letters), Sep. 1, 2003, vol. 83, No. 9, pp. 1755-1757.
- Nomura.K et al., "Carrier transport in transparent oxide semiconductor with intrinsic structural randomness probed using single-crystalline InGaO₃(ZnO)₅ films", Appl. Phys. Lett. (Applied Physics Letters), Sep. 13, 2004, vol. 85, No. 11, pp. 1993-1995.
- Terai.Y et al., "A Polycrystalline Oxide TFT Driven AM-OLED Display", IDW'11: Proceedings of the 18th International Display Workshops, Dec. 7, 2011, pp. 61-64.
- Nakayama et al., "17a-TL-8 Effect of GaO Layer on IGZO-TFT Channel," Extended Abstracts (The 57th Spring Meeting 2010), The Japan Society of Applied Physics and Related Societies, Mar. 17, 2010, pp. 21-008.

* cited by examiner

FIG. 1A

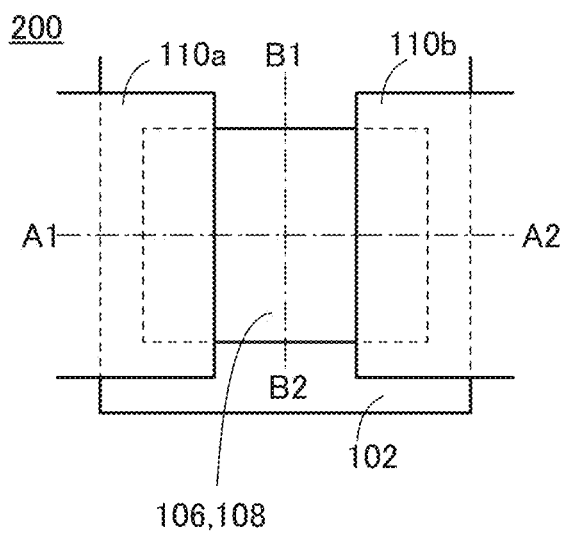


FIG. 1B

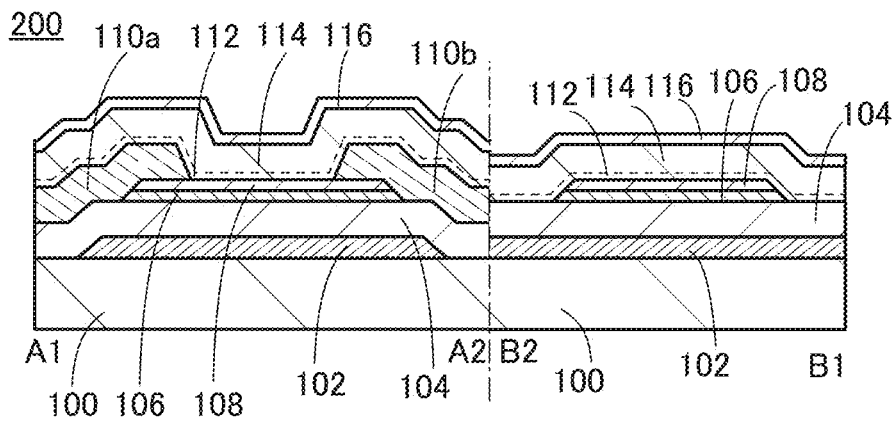


FIG. 2A

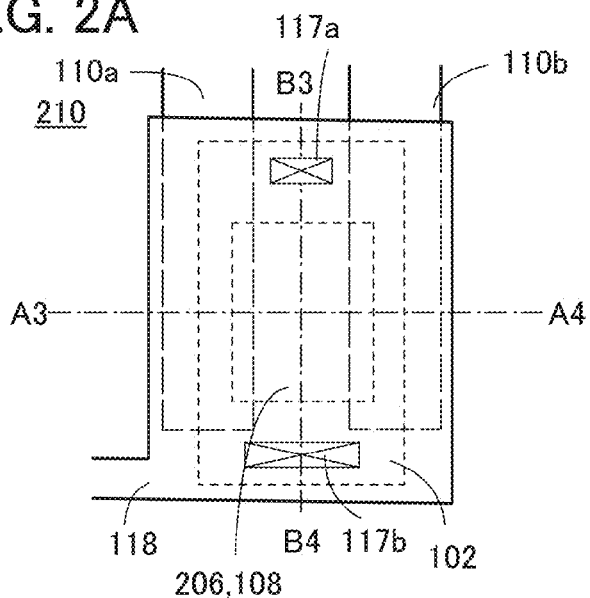


FIG. 2B

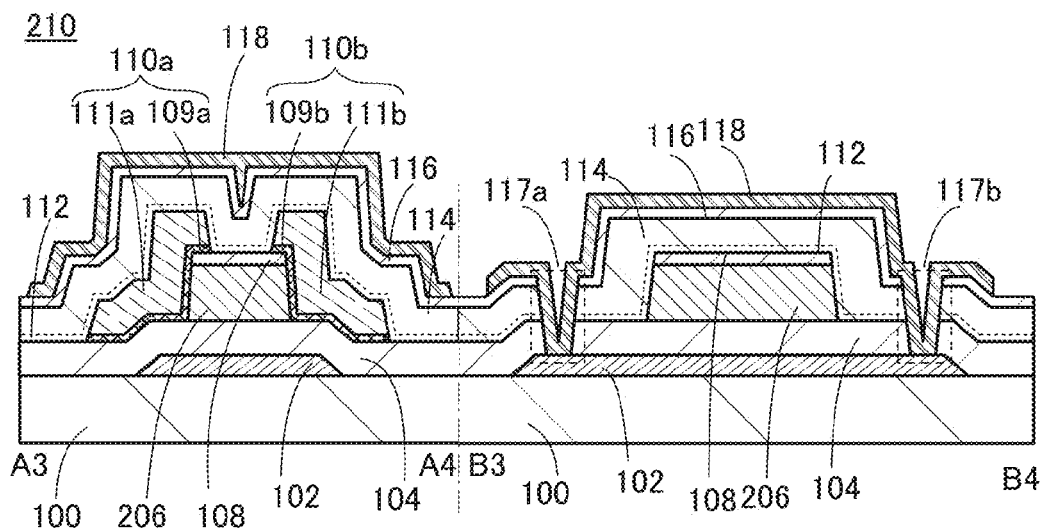


FIG. 3A

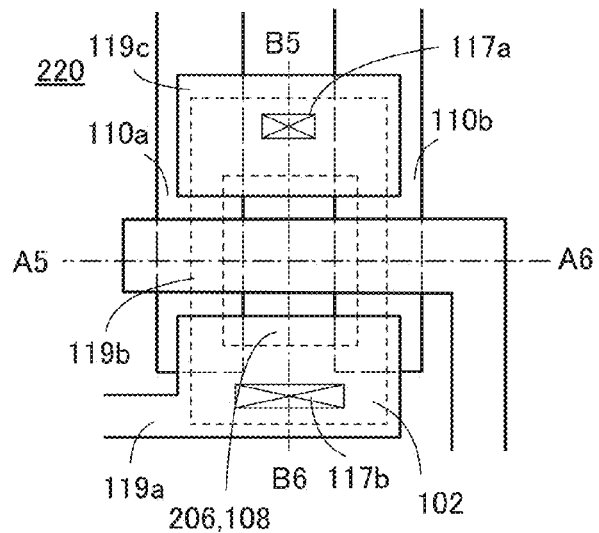


FIG. 3B

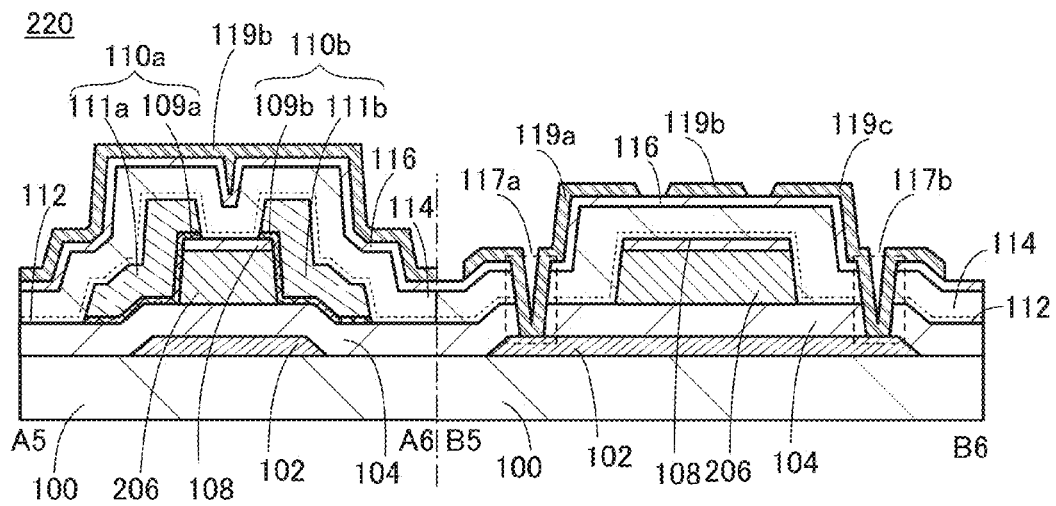


FIG. 4A

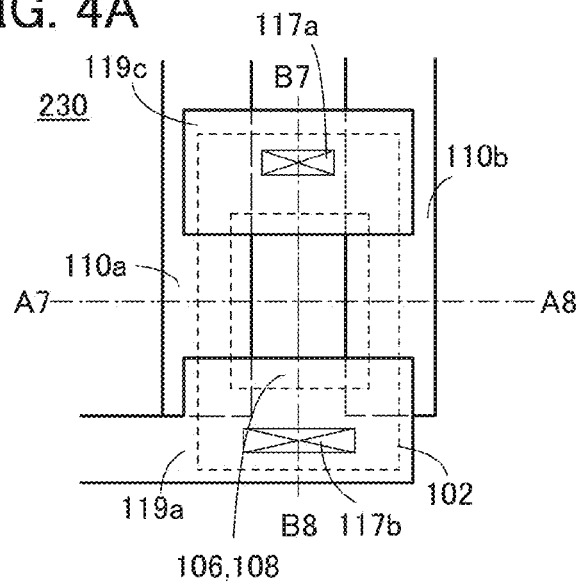


FIG. 4B

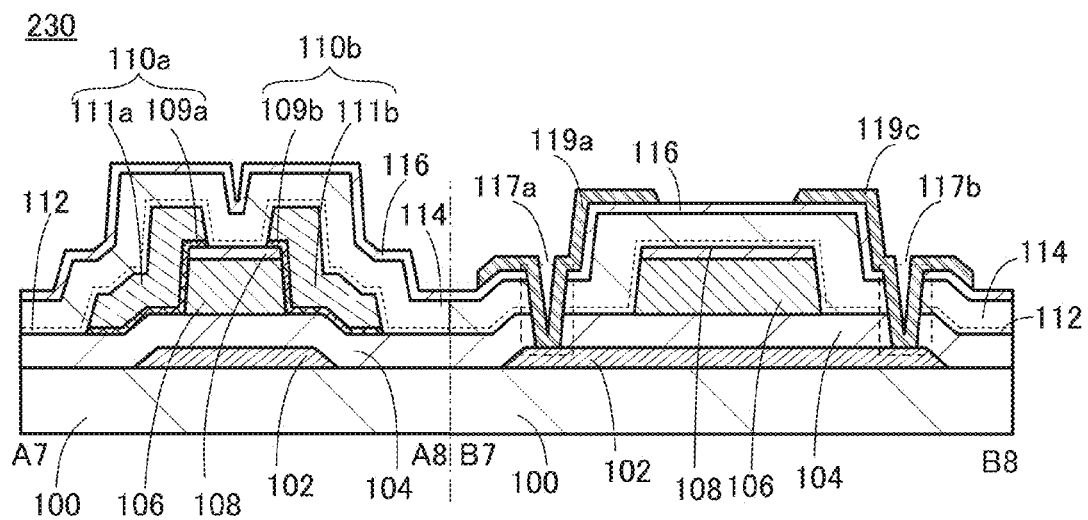


FIG. 5A

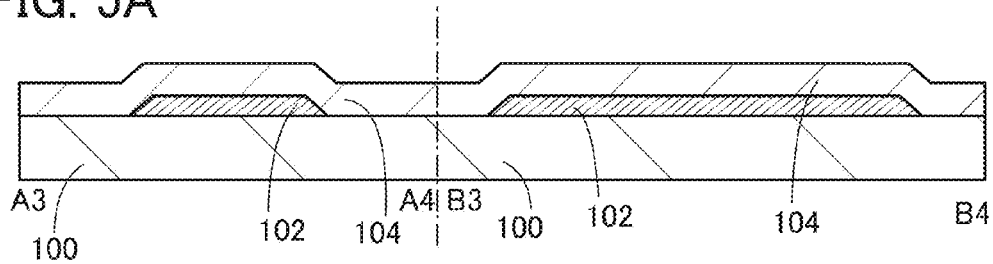


FIG. 5B

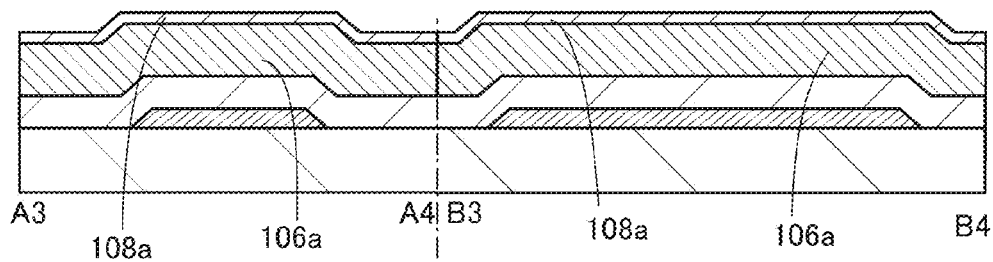


FIG. 5C

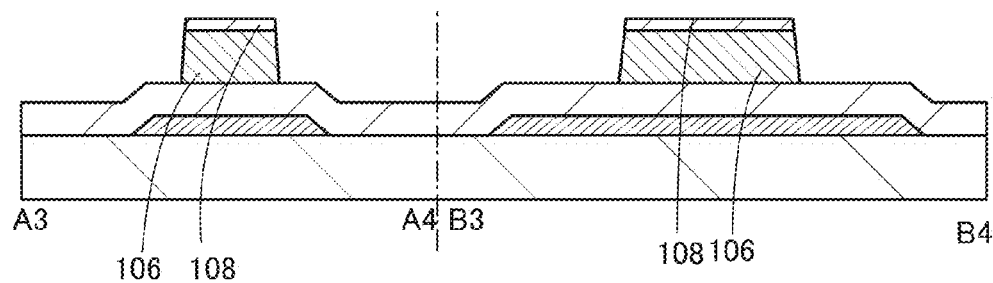


FIG. 5D

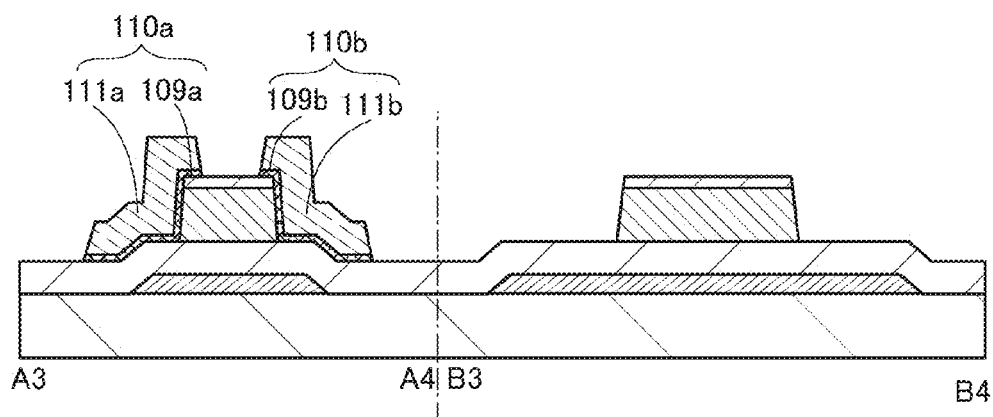


FIG. 6A

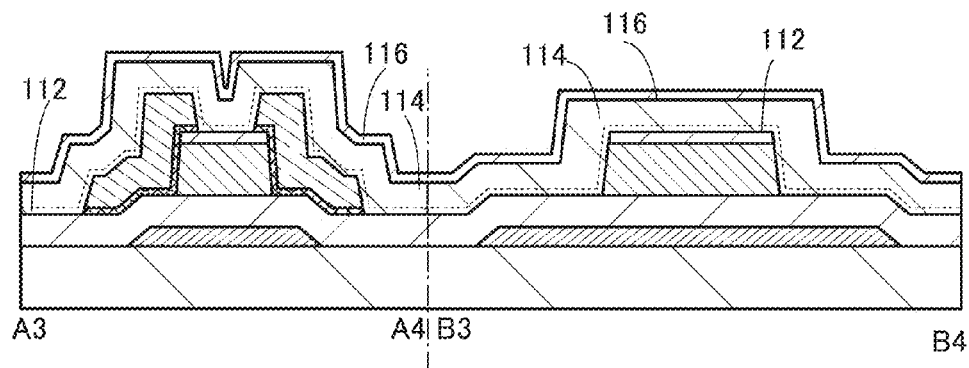


FIG. 6B

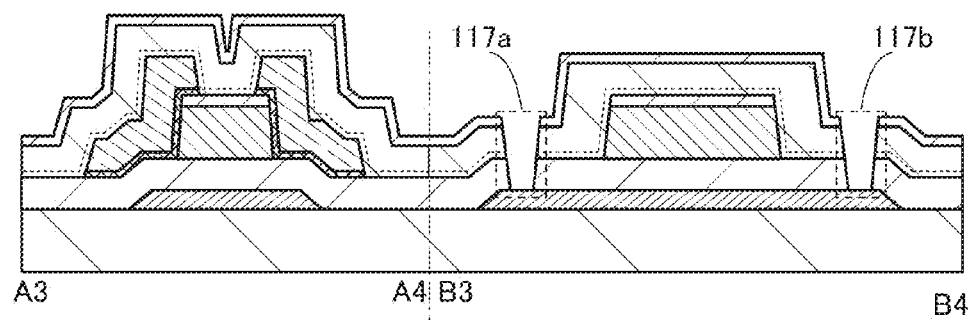


FIG. 6C

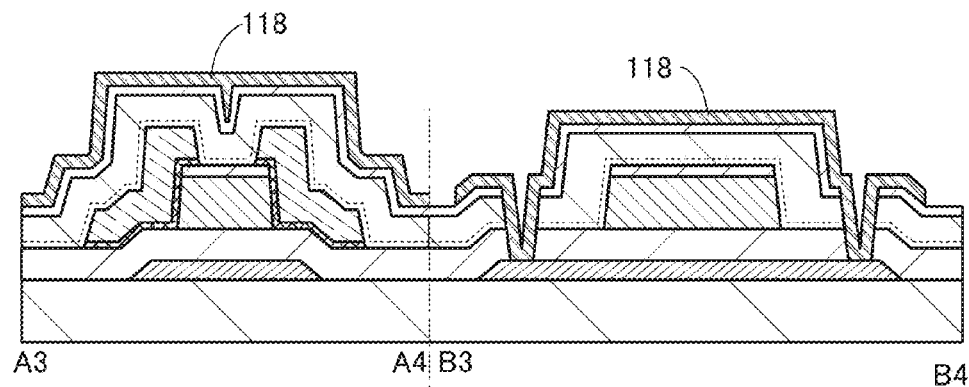


FIG. 7A

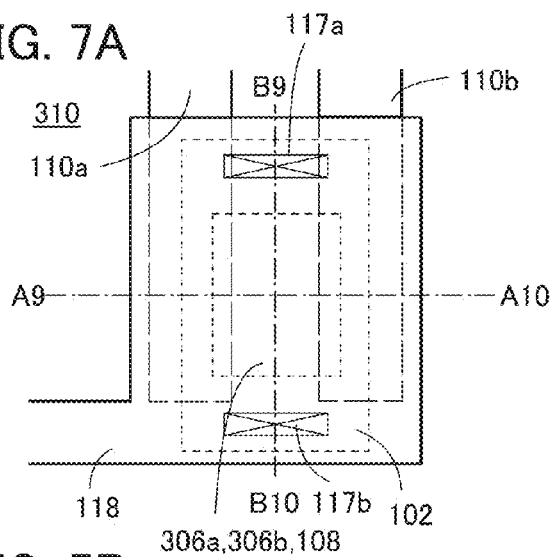


FIG. 7B

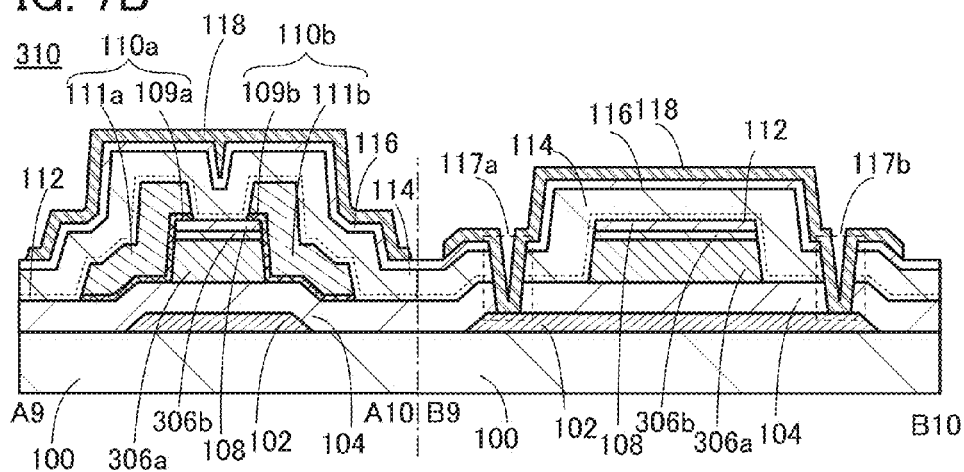


FIG. 7C

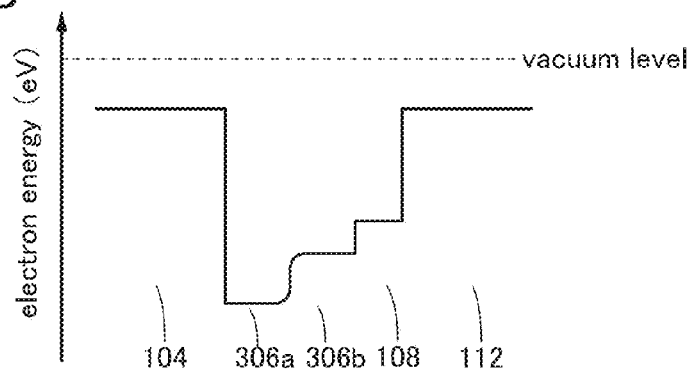


FIG. 8A

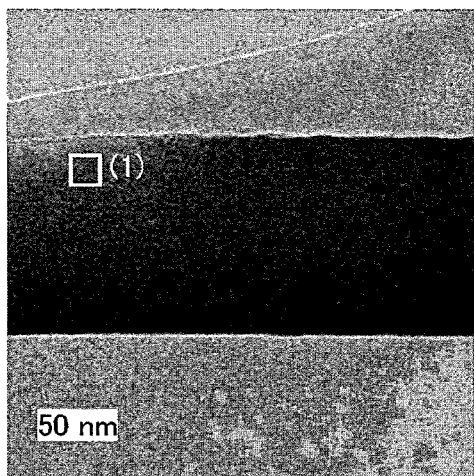


FIG. 8B

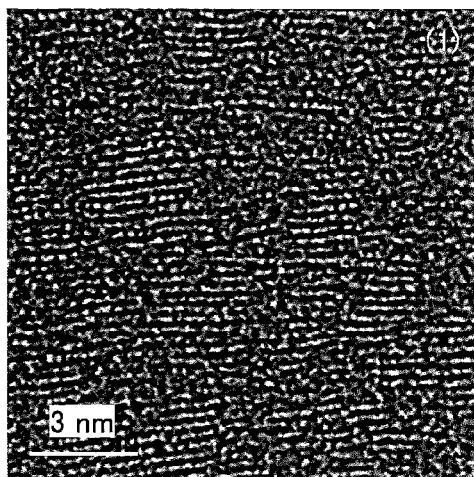


FIG. 8C

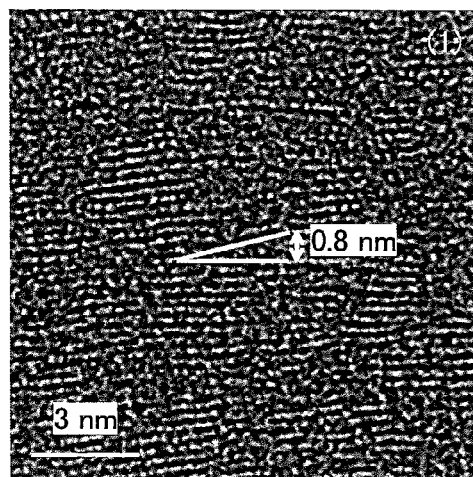


FIG. 8D

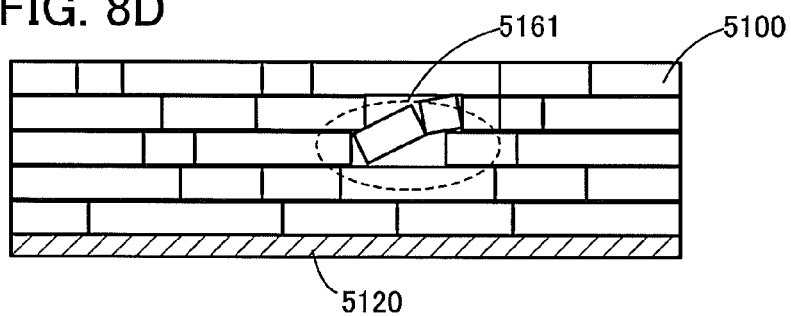
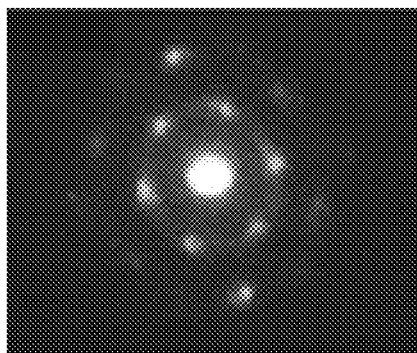
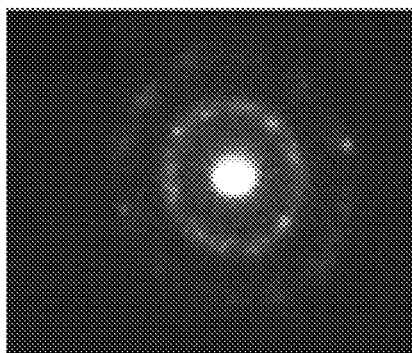


FIG. 9A



CAAC-OS

FIG. 9B



nc-OS

FIG. 9C

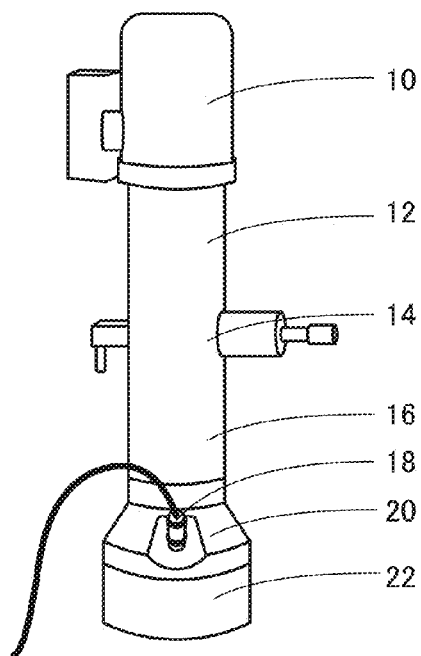


FIG. 9D

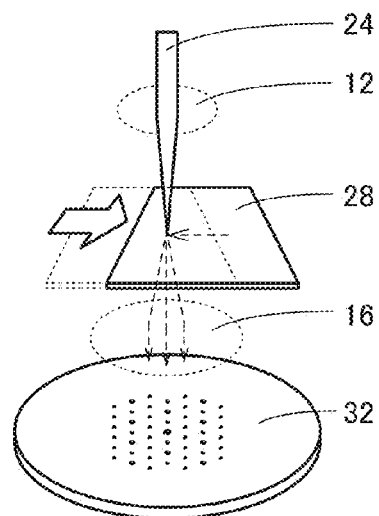


FIG. 10A

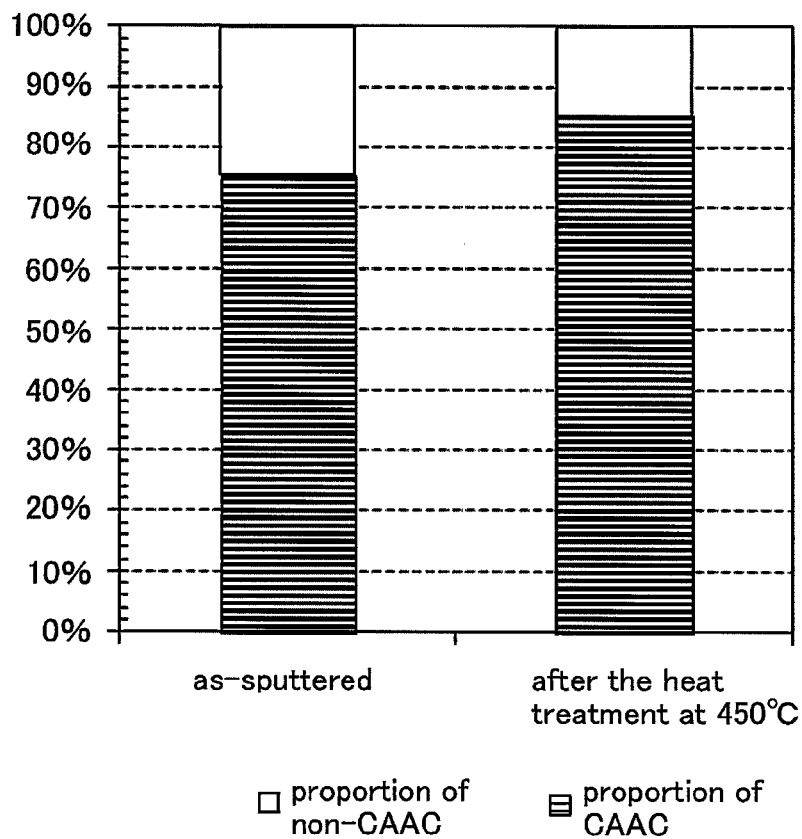
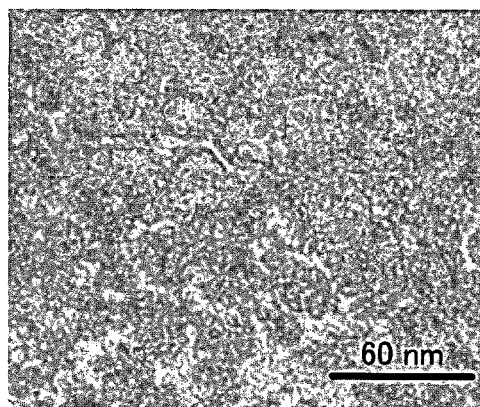
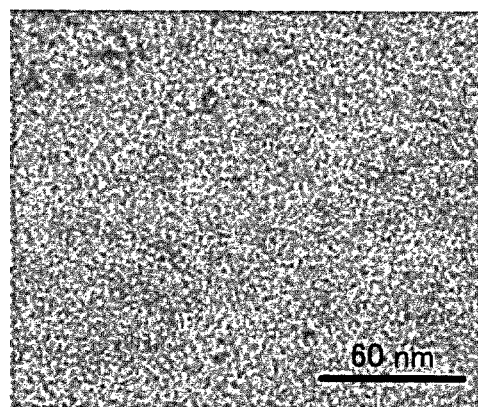


FIG. 10B



as-sputtered

FIG. 10C



after the heat treatment at 450°C

FIG. 11A

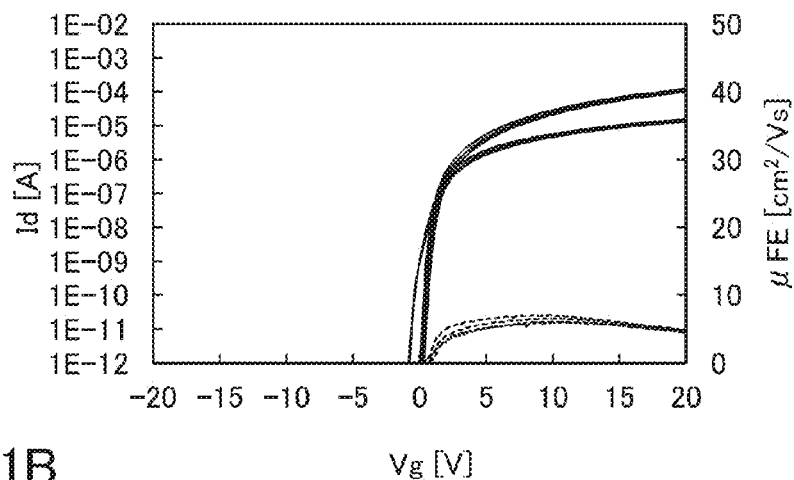


FIG. 11B

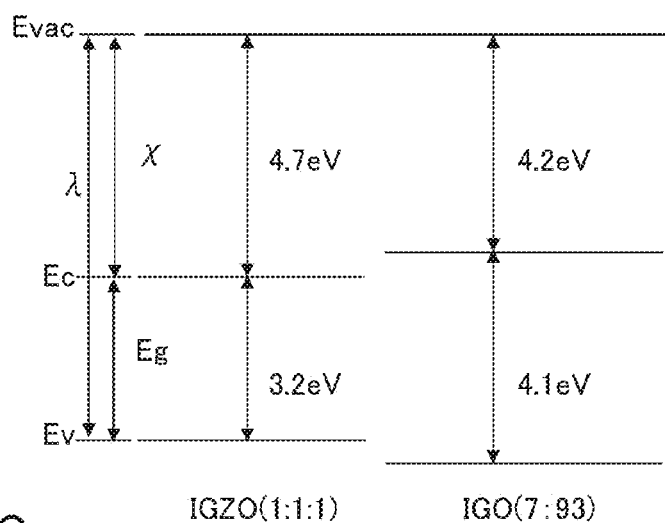


FIG. 11C

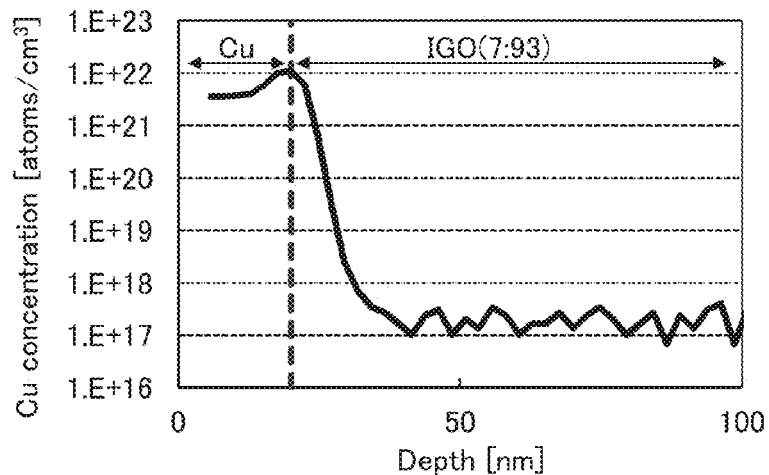


FIG. 12A

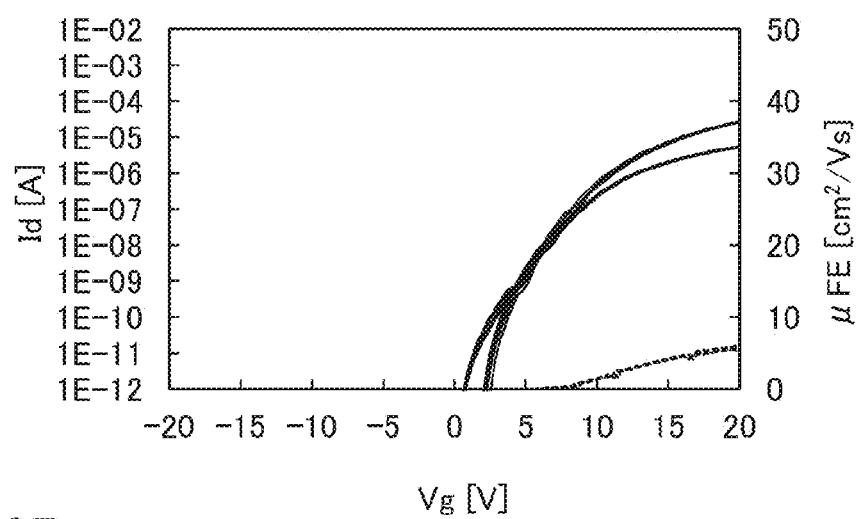


FIG. 12B

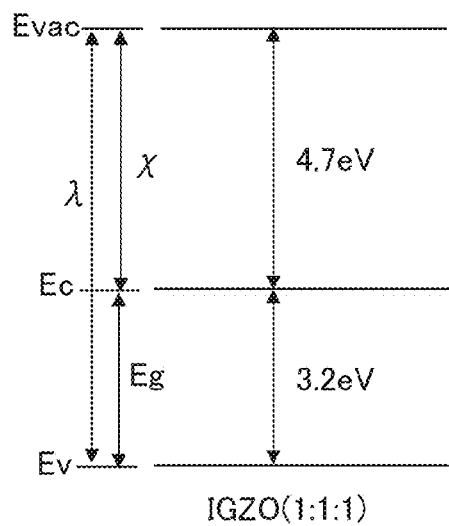


FIG. 13A

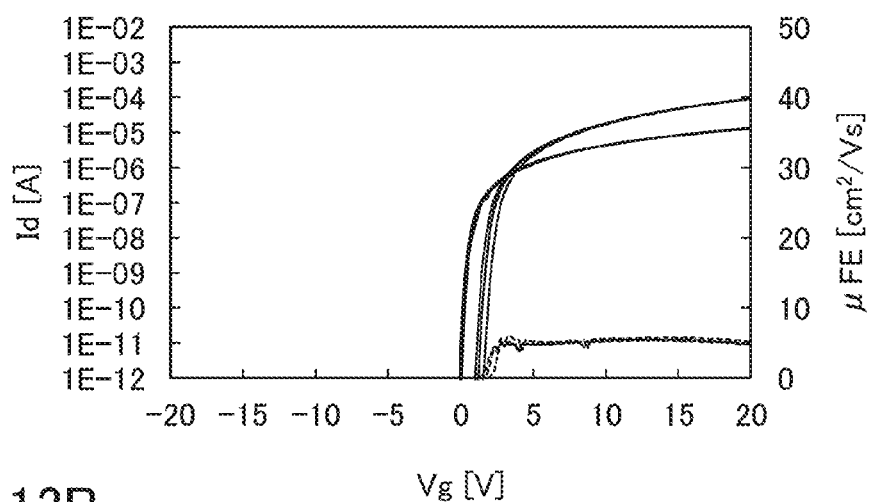


FIG. 13B

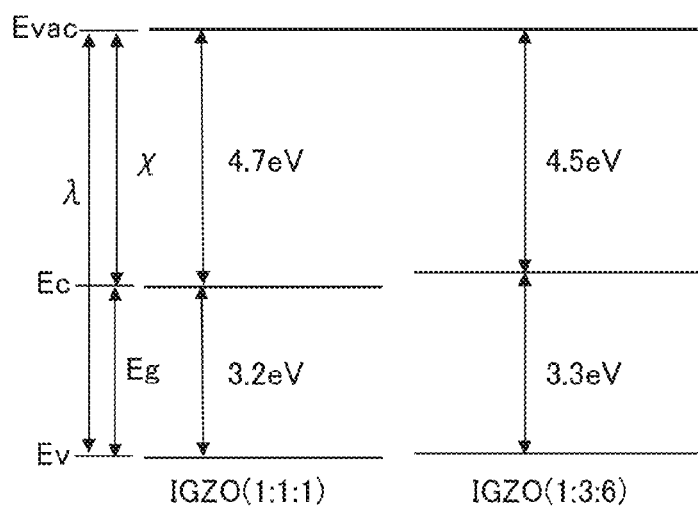


FIG. 13C

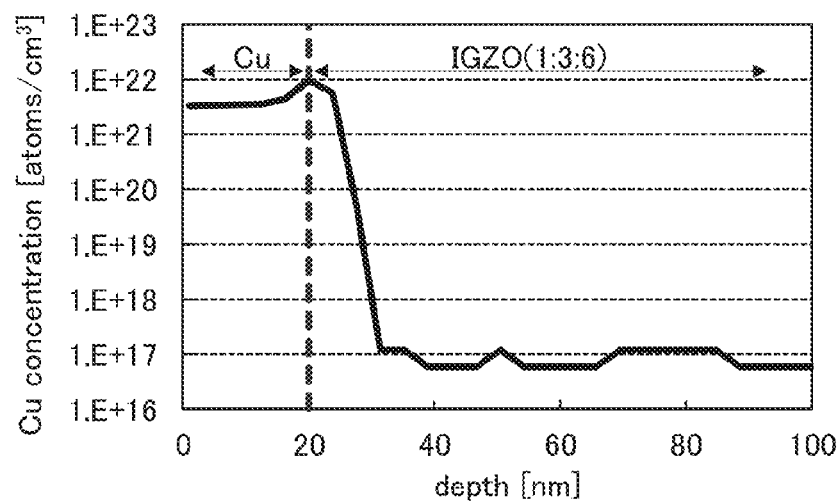


FIG. 14A

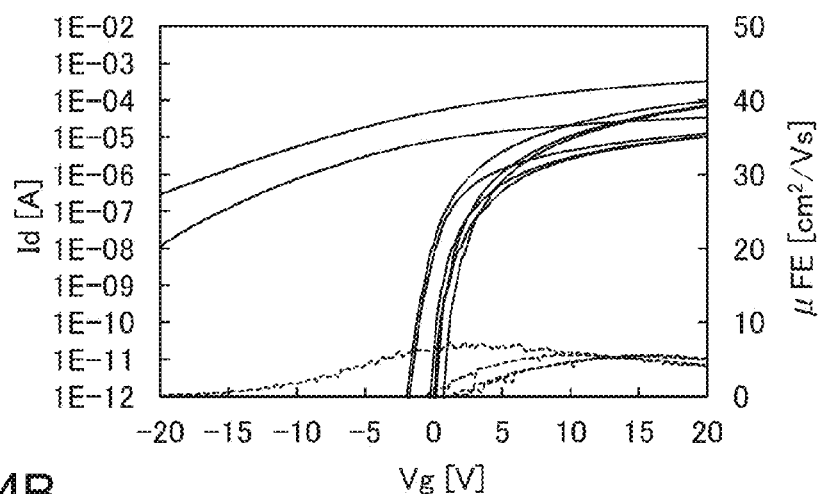


FIG. 14B

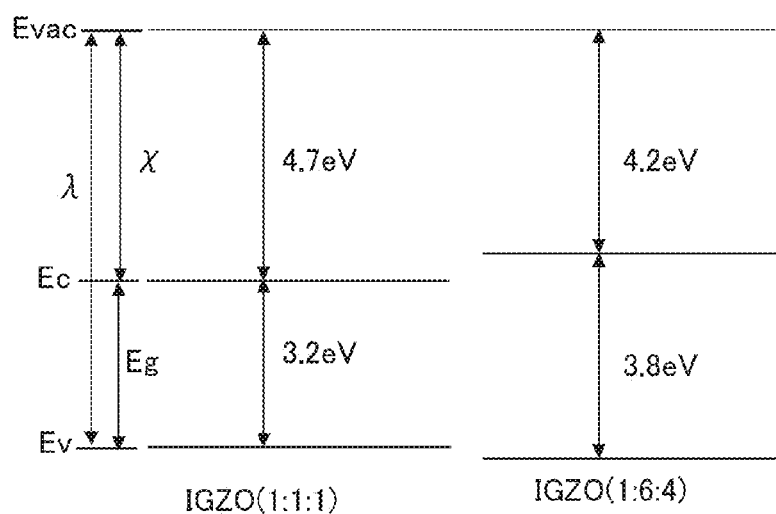


FIG. 14C

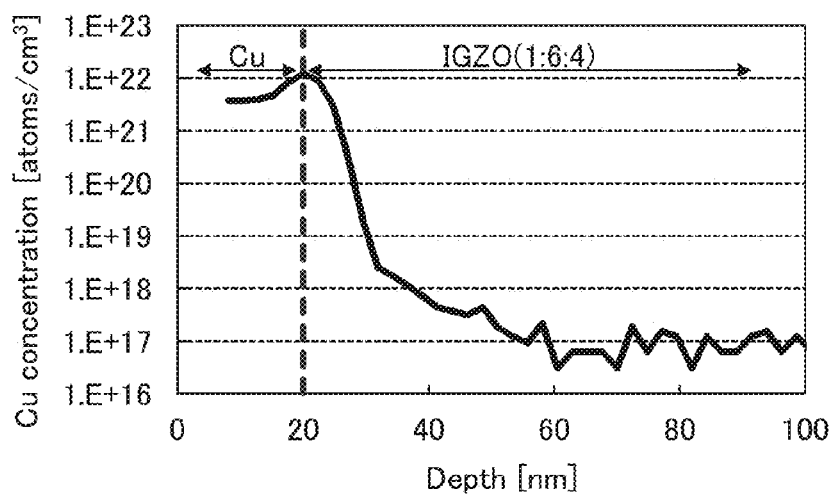


FIG. 15A

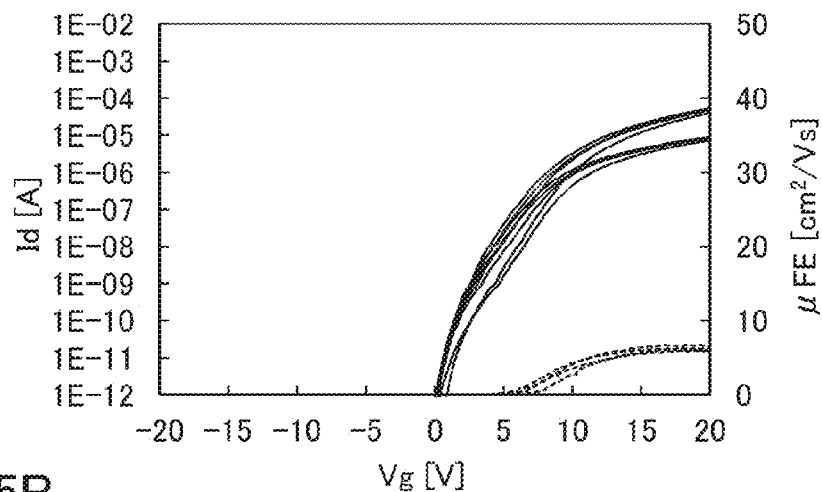


FIG. 15B

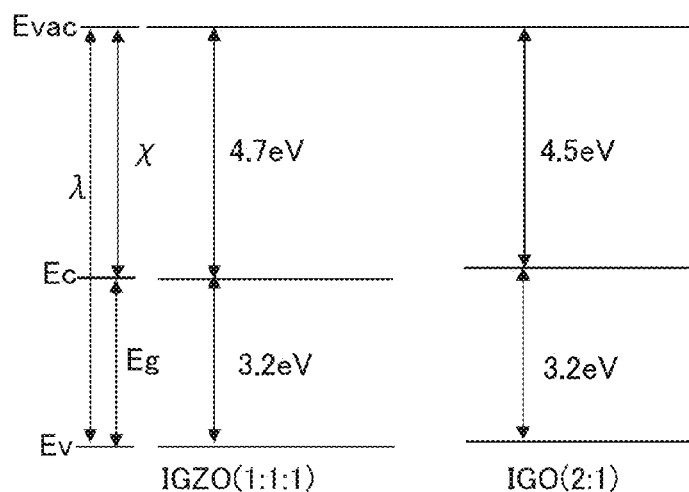


FIG. 15C

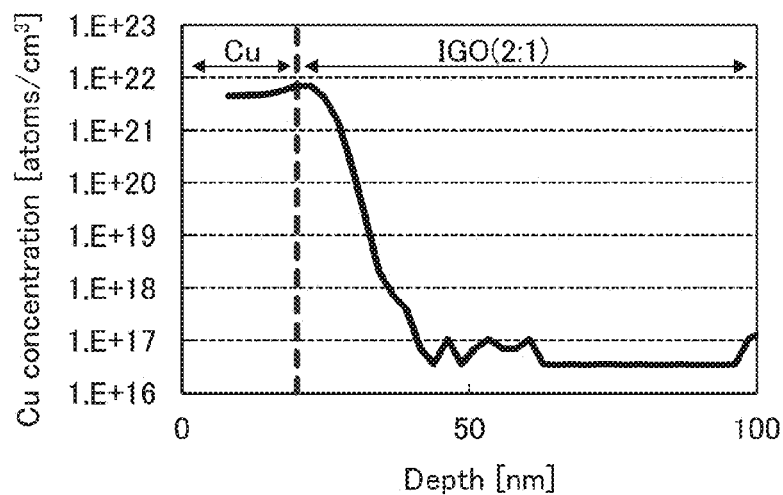


FIG. 16

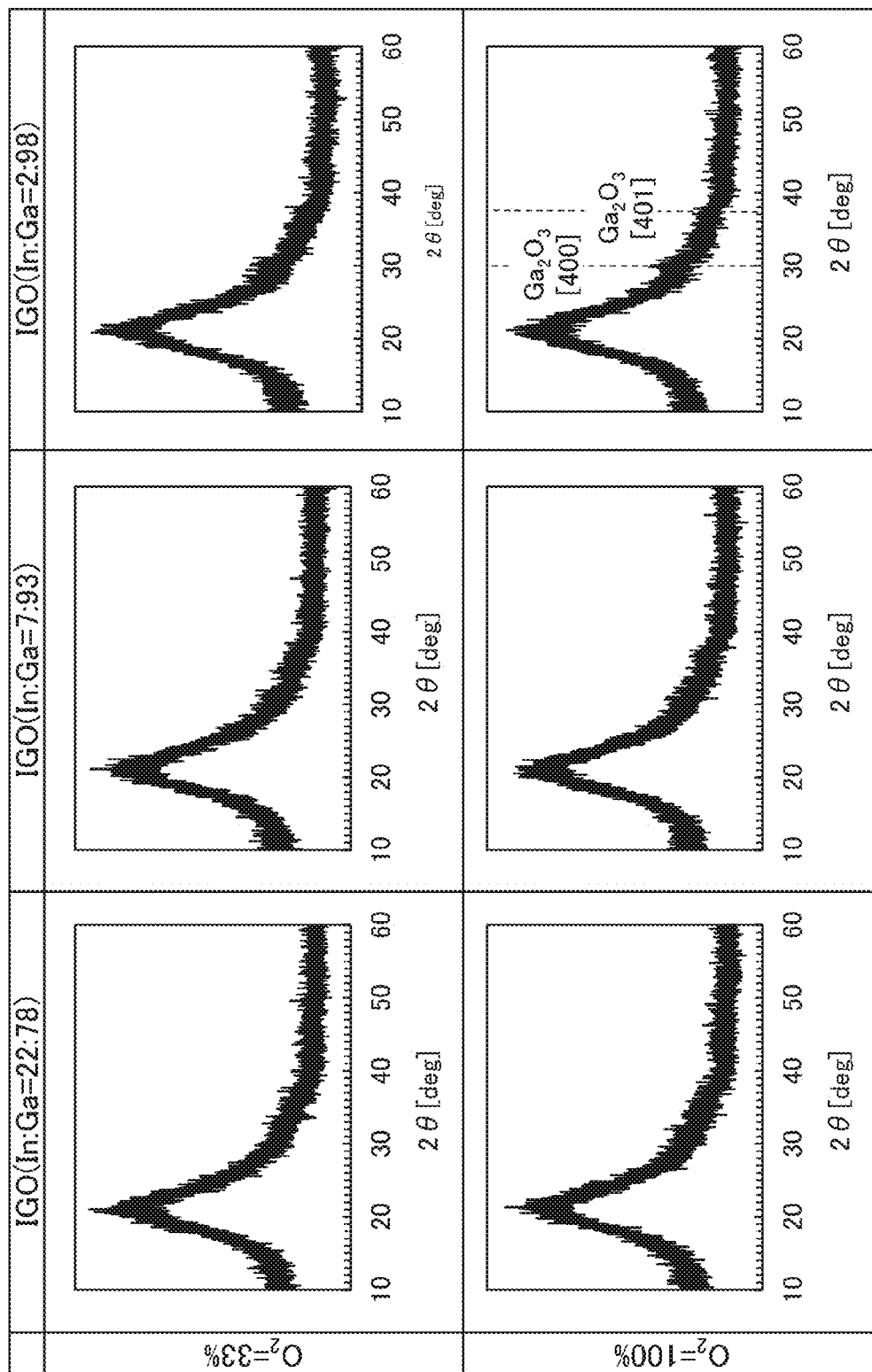


FIG. 17

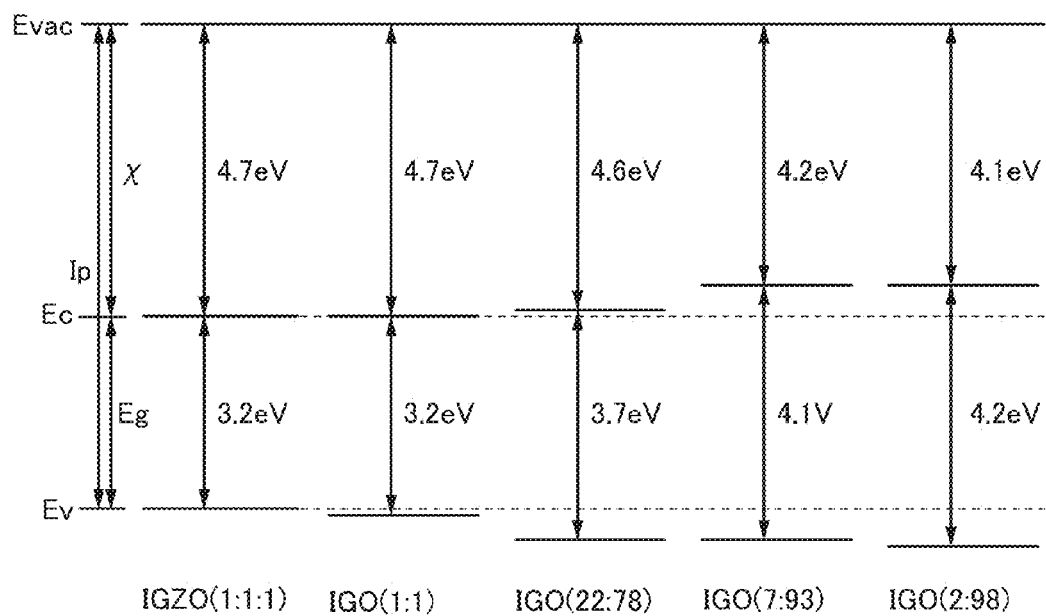


FIG. 18A

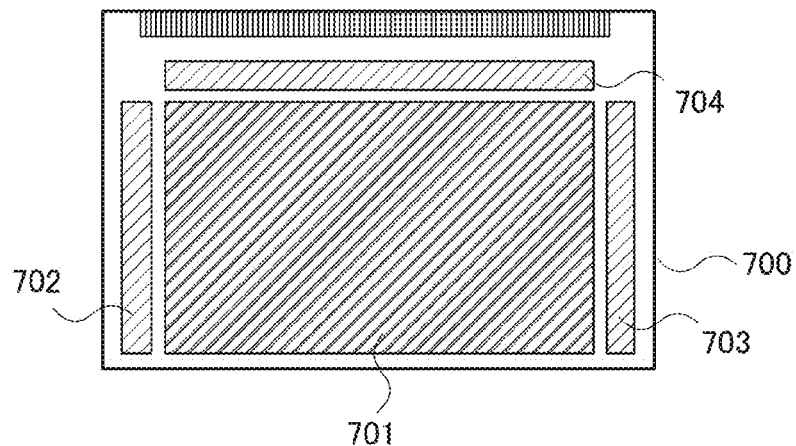


FIG. 18B

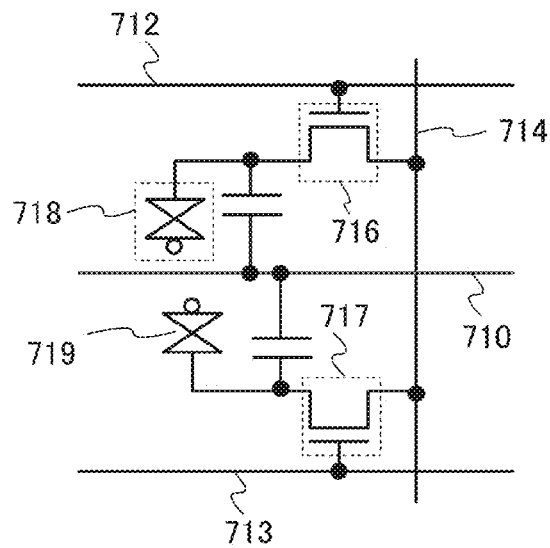


FIG. 18C

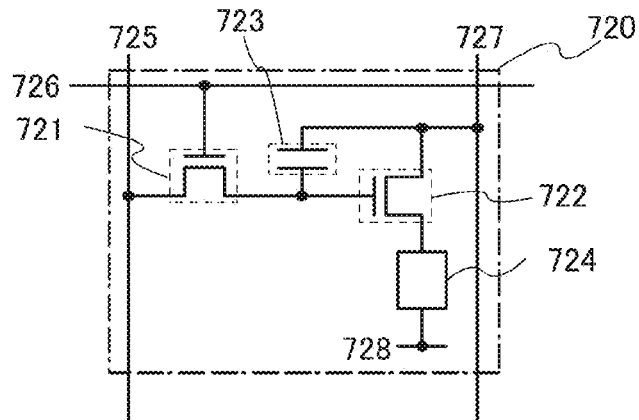


FIG. 19

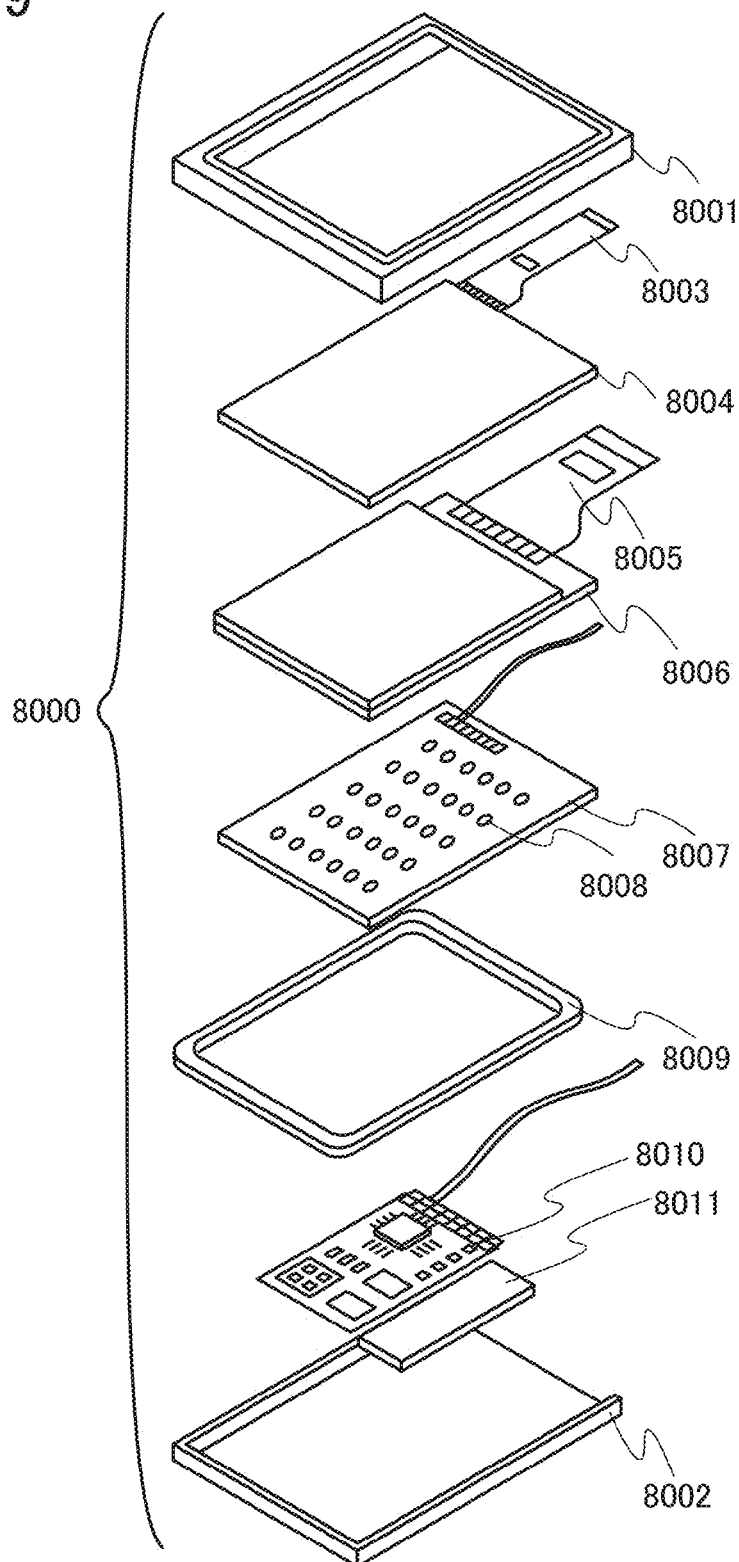


FIG. 20A

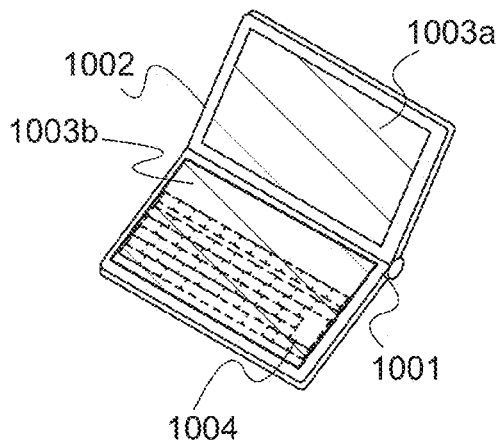


FIG. 20B

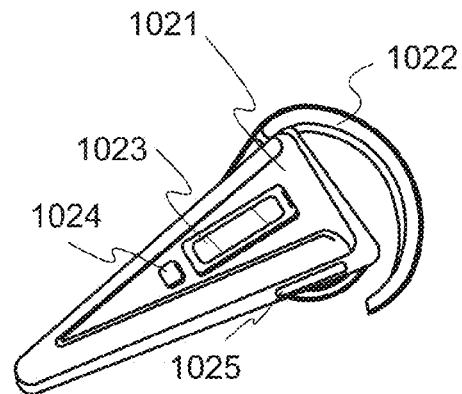


FIG. 20C

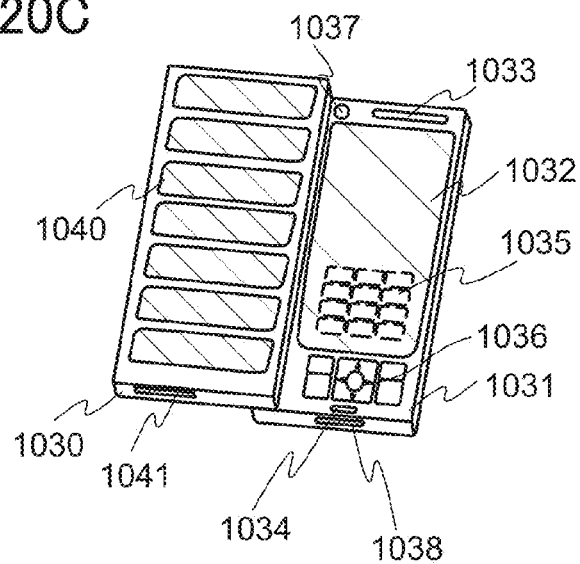


FIG. 20D

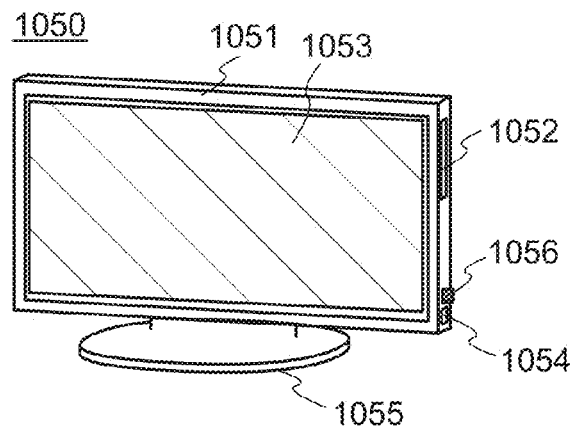


FIG. 21A

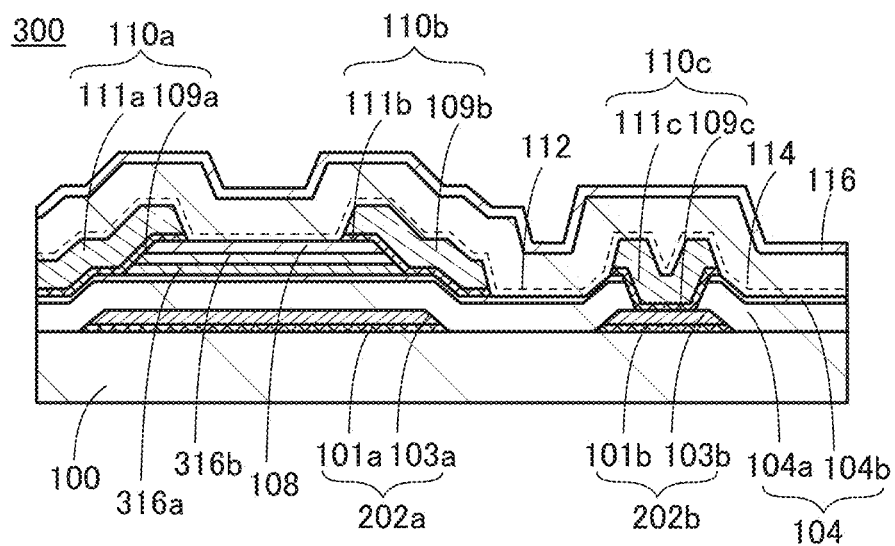


FIG. 21B

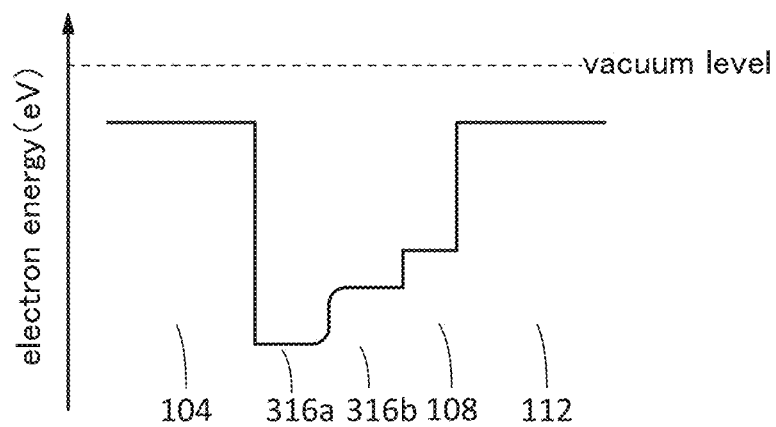


FIG. 22A

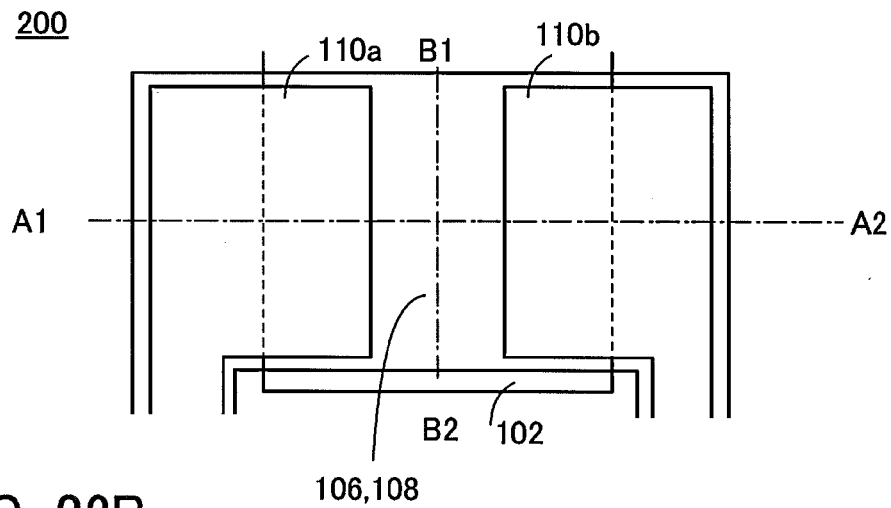


FIG. 22B

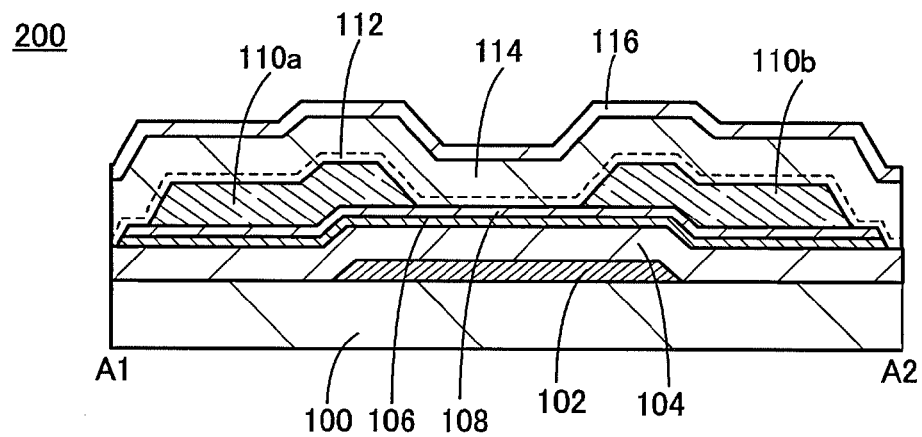


FIG. 22C

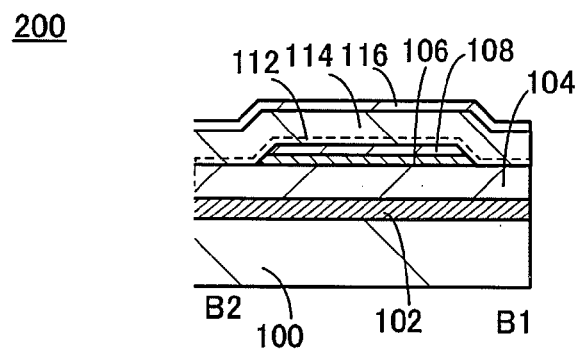


FIG. 23A

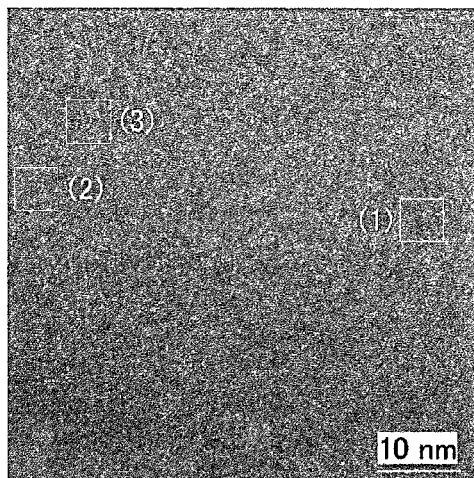


FIG. 23B

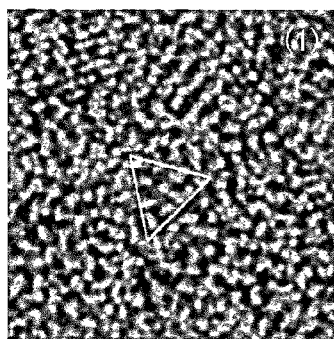


FIG. 23C

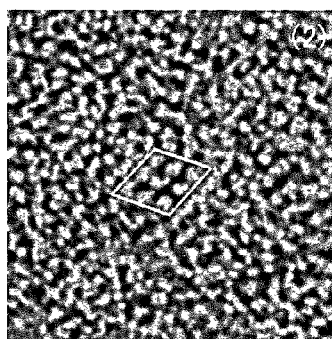


FIG. 23D

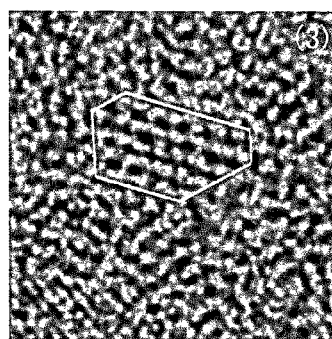


FIG. 24A

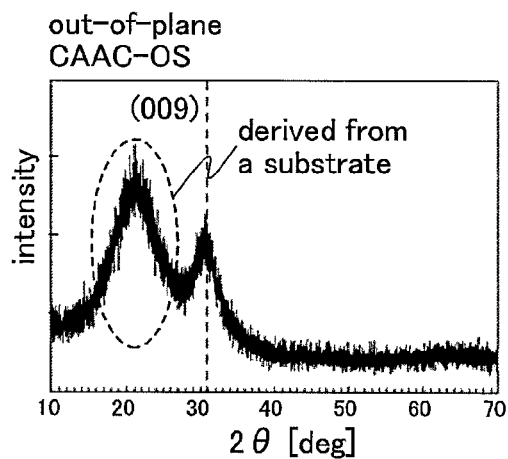


FIG. 24B

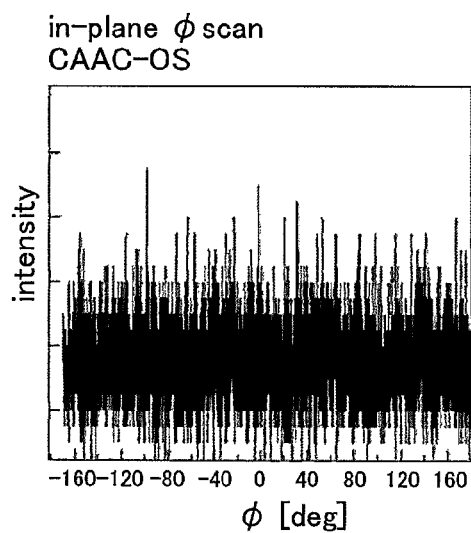


FIG. 24C

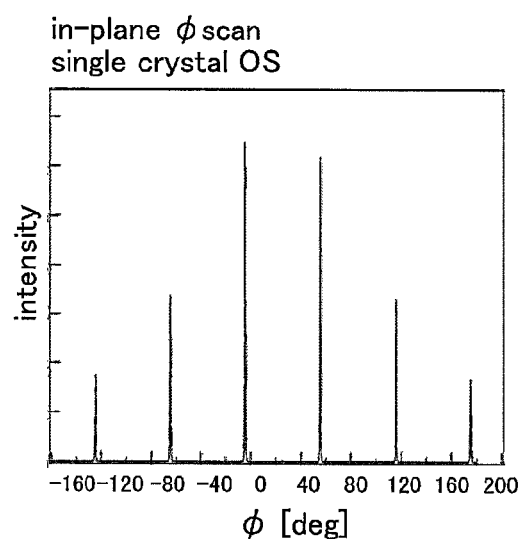


FIG. 25A

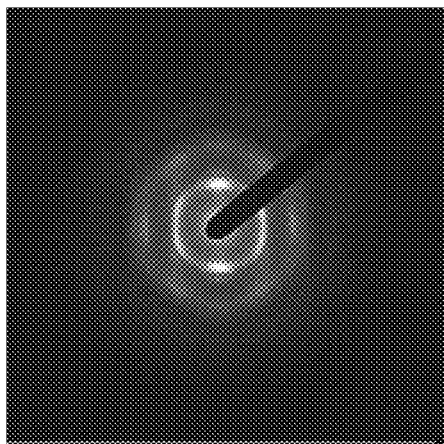


FIG. 25B

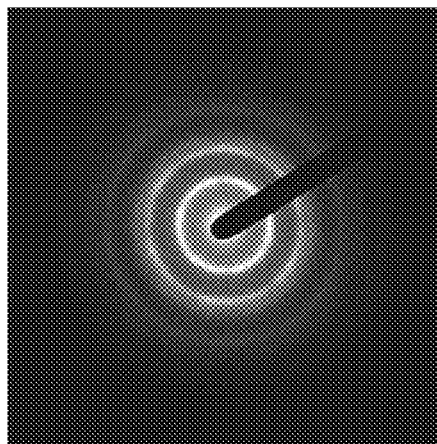


FIG. 26

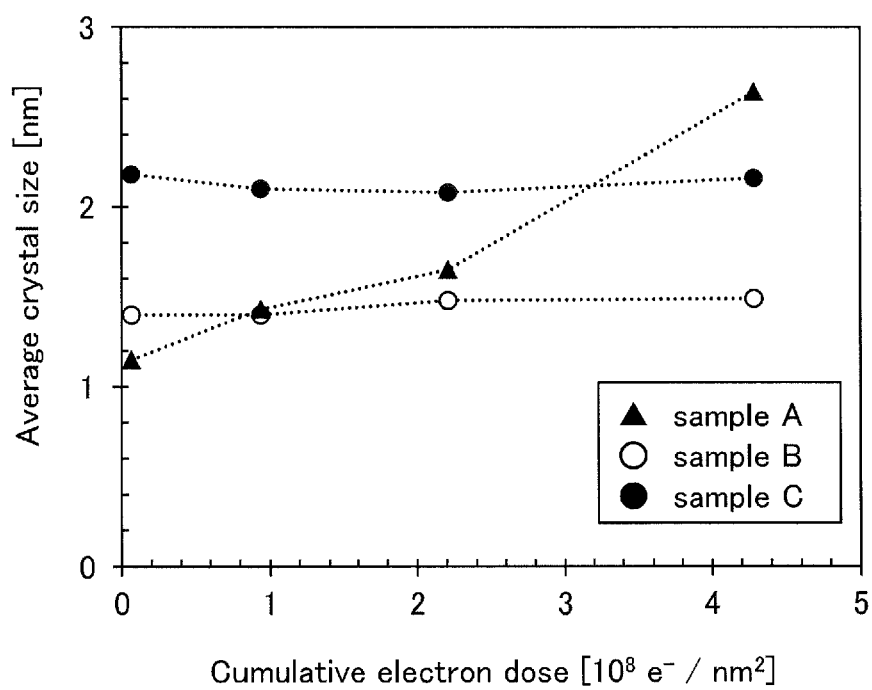


FIG. 27A

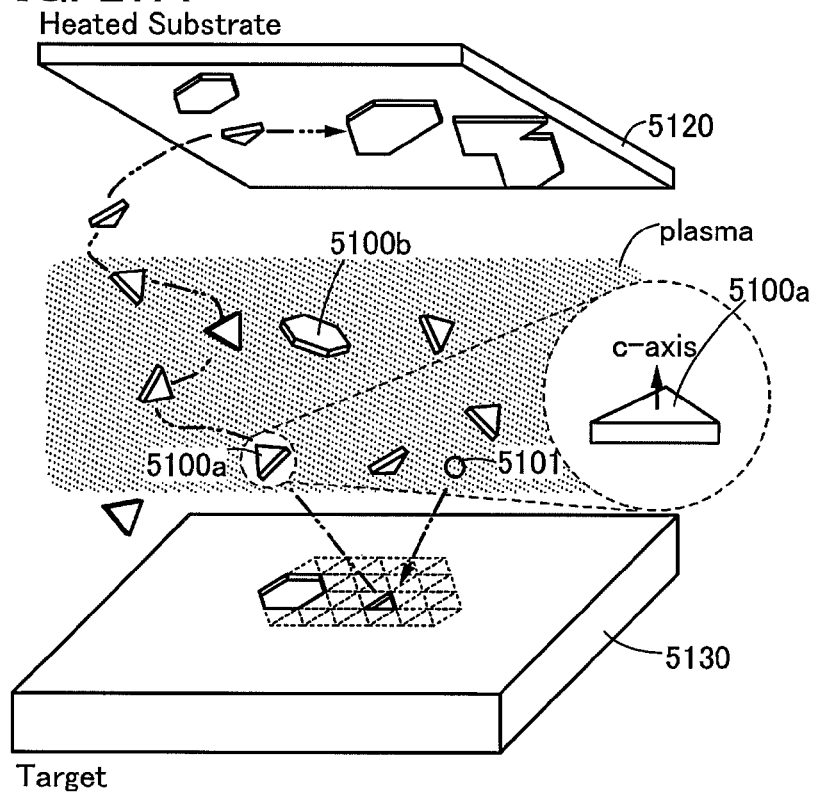


FIG. 27B

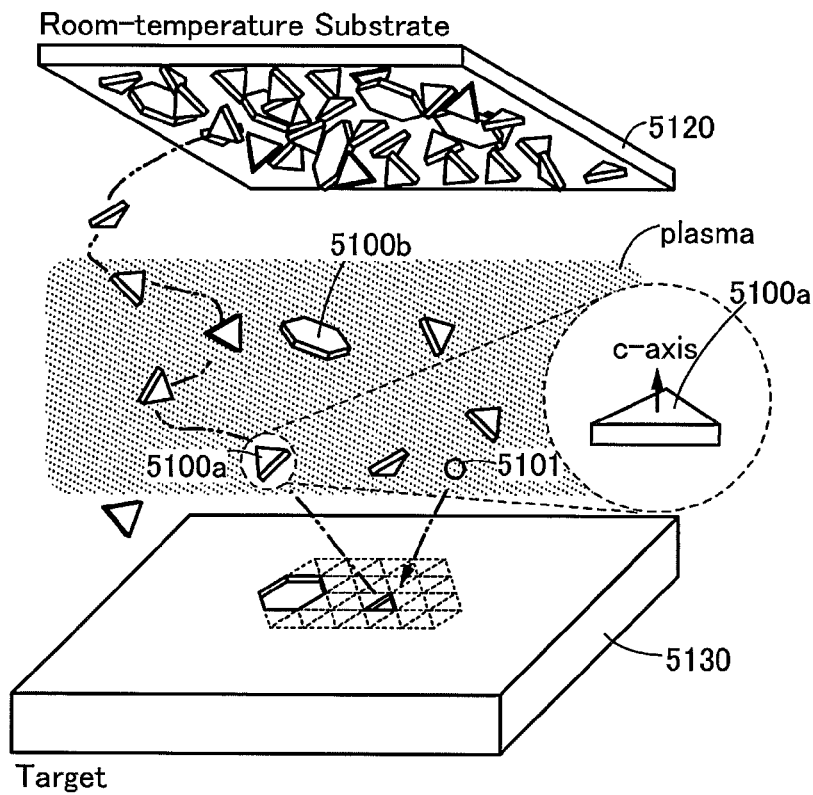


FIG. 28A

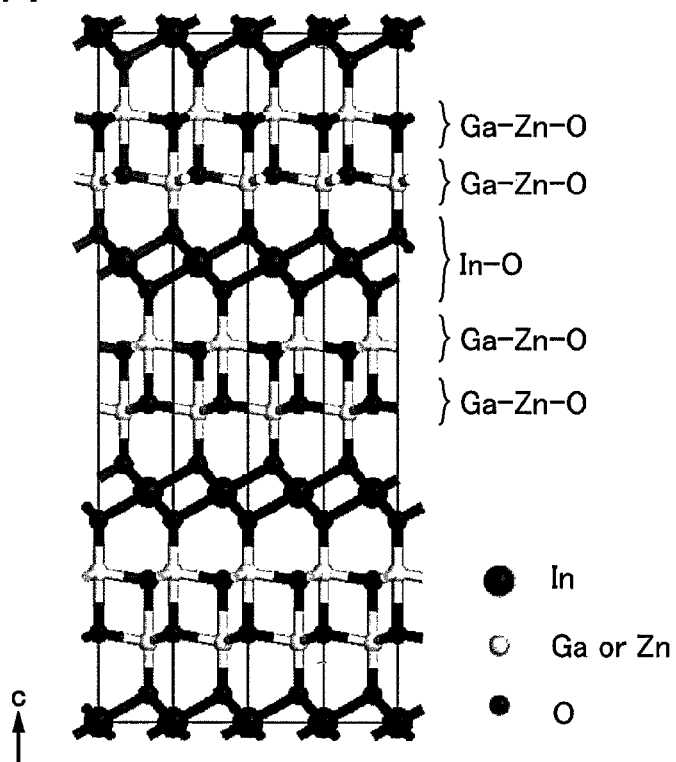


FIG. 28B

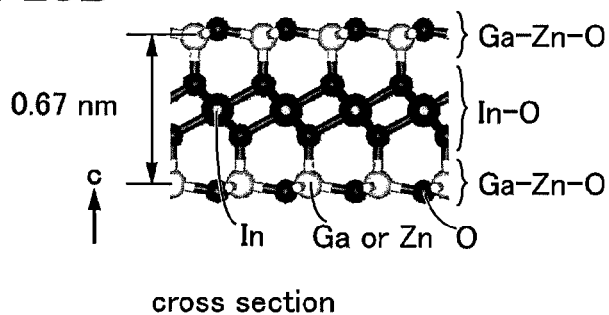


FIG. 28C

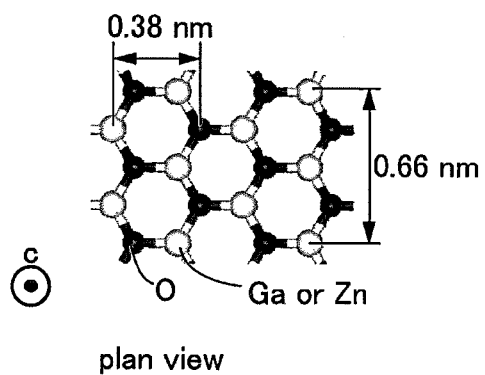


FIG. 29A

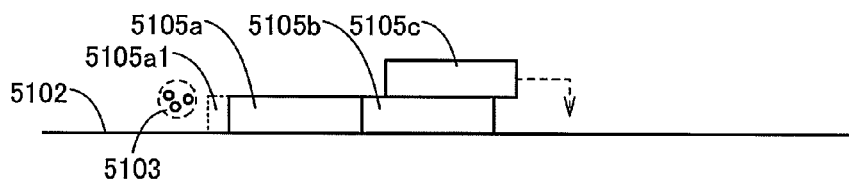


FIG. 29B

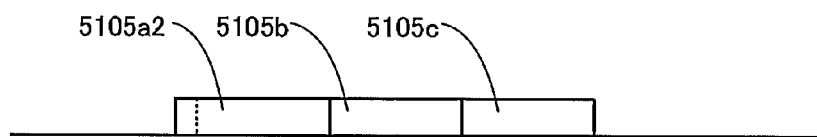


FIG. 29C

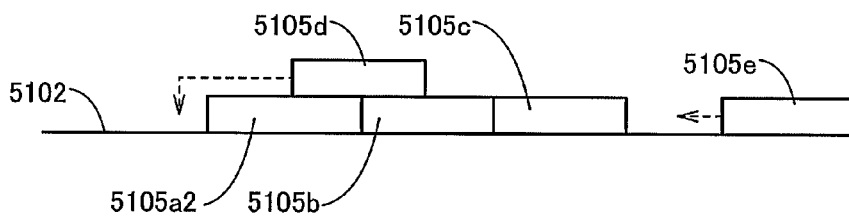
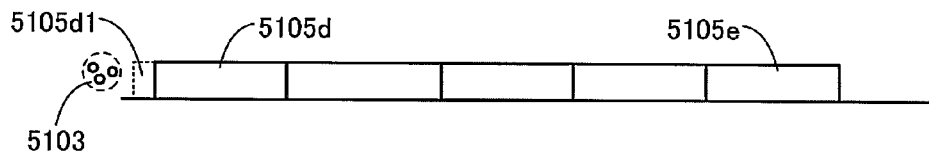


FIG. 29D



SEMICONDUCTOR DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an object, a method, or a manufacturing method. In addition, the present invention relates to a process, a machine, manufacture, or a composition of matter. One embodiment of the present invention particularly relates to a semiconductor device and a method for manufacturing the semiconductor device.

In this specification and the like, a semiconductor device generally means a device that can function by utilizing semiconductor characteristics. An electro-optical device, an image display device (also simply referred to as a display device), a semiconductor circuit, a light-emitting device, a power storage device, a memory device, and an electronic appliance may include a semiconductor device.

2. Description of the Related Art

As semiconductor materials of transistors used for most display devices typified by liquid crystal display devices and light-emitting display devices and most integrated circuits (ICs), silicon semiconductors such as amorphous silicon, single crystal silicon, and polycrystalline silicon are known. Furthermore, as other semiconductor materials, oxide semiconductors have been attracting attention. For example, a technique for applying a transistor in which zinc oxide or In—Ga—Zn-based oxide is used as an oxide semiconductor for a channel, to a display device, is disclosed (Patent Document 1). Furthermore, a technique to apply a transistor in which polycrystalline In—Ga oxide is used as an oxide semiconductor for a channel, to a display device, is disclosed (Non-Patent Document 1).

In addition, to reduce wiring delay due to increase in wiring resistance and parasitic capacitance caused by increase in size and definition of a display device, a technique to form a wiring using a low-resistance material such as copper, aluminum, gold, or silver is considered (Patent Document 2).

REFERENCE

Patent Document

[Patent Document 1] Japanese Published Patent Application No. 2007-096055

[Patent Document 2] Japanese Published Patent Application No. 2004-133422

Non-Patent Document

[Non-Patent Document 1] Yasuhiro Terai et al., "A Polycrystalline Oxide TFT Driven AM-OLED Display", IDW'11, pp. 61-64

SUMMARY OF THE INVENTION

In a transistor including an oxide semiconductor, a large amount of impurity (typically, silicon, which is a constituent element of an insulating layer; carbon; and copper, which is a constituent material of a wiring) contained in an oxide semiconductor layer causes a reduction in electrical characteristics (e.g., on-state current characteristics) of the transistor.

Another object of one embodiment of the present invention is to reduce the concentration of impurity contained in an oxide semiconductor layer of a semiconductor device such as a transistor including an oxide semiconductor. Another object of one embodiment of the present invention is to improve

electrical characteristics of a semiconductor device or the like including an oxide semiconductor. Another object of one embodiment of the present invention is to improve the reliability of a semiconductor device or the like including an oxide semiconductor. Another object of one embodiment of the present invention is to provide a novel semiconductor device or the like.

Note that the description of these objects does not disturb the description of other objects. One embodiment of the present invention does not necessarily achieve all the objects. Objects other than the above objects will be apparent from and can be derived from the description of the specification and the like.

One embodiment of the present invention is a semiconductor device including an oxide semiconductor layer; a metal oxide layer in contact with the oxide semiconductor layer, the metal oxide layer including an In-M oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf); and a conductive layer in contact with the metal oxide layer, the conductive layer including copper, aluminum, gold, or silver. In the semiconductor device, $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where the atomic ratio of In to M included in the metal oxide layer is In:M=x:y.

Another embodiment of the present invention is a semiconductor device including a gate electrode layer, a gate insulating layer in contact with the gate electrode layer, an oxide semiconductor layer facing the gate electrode layer with the gate insulating layer positioned between the gate electrode layer and the oxide semiconductor layer; a metal oxide layer in contact with the oxide semiconductor layer, the metal oxide layer including an In-M oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf); and a pair of electrode layers in contact with the metal oxide layer, the pair of electrode layers including copper, aluminum, gold, or silver. In the semiconductor device, $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where the atomic ratio of In to M included in the metal oxide layer is In:M=x:y.

Another embodiment of the present invention is a semiconductor device including a first gate electrode layer, a first gate insulating layer in contact with the first gate electrode layer; an oxide semiconductor layer facing the first gate electrode layer with the first gate insulating layer positioned between the first gate electrode layer and the oxide semiconductor layer; a metal oxide layer in contact with the oxide semiconductor layer, the metal oxide layer including an In-M oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf); a pair of electrode layers in contact with the metal oxide layer, the pair of electrode layers including copper, aluminum, gold, or silver; a second gate insulating layer over and in contact with the pair of electrode layers; and a second gate electrode layer facing the oxide semiconductor layer with the second gate insulating layer positioned between the oxide semiconductor layer and the second gate electrode layer. In the semiconductor device, $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where the atomic ratio of In to M included in the metal oxide layer is In:M=x:y, and the first gate electrode layer and the second gate electrode layer are electrically connected to each other through an opening portion formed in the first gate insulating layer and the second gate insulating layer.

In the semiconductor device, the oxide semiconductor layer may include a first side surface and a second side surface in contact with the pair of electrodes, and a third side surface and a fourth side surface facing the first gate electrode layer or the second gate electrode layer.

In the semiconductor device, gallium is preferably contained as the element M.

In the semiconductor device, the oxide semiconductor layer may have a stacked-layer structure including a first oxide semiconductor layer and a second oxide semiconductor layer between the first oxide semiconductor layer and the metal oxide layer. In that case, the electron affinity of the second oxide semiconductor layer is preferably smaller than the electron affinity of the first oxide semiconductor layer and preferably larger than the electron affinity of the metal oxide layer.

In this specification, a term “parallel” indicates that the angle formed between two straight lines is greater than or equal to -10° and less than or equal to 10° , and accordingly also includes the case where the angle is greater than or equal to -5° and less than or equal to 5° . The term “substantially parallel” indicates that the angle formed between two straight lines is greater than or equal to -30° and less than or equal to 30° . The term “perpendicular” indicates that the angle formed between two straight lines is greater than or equal to 80° and less than or equal to 100° , and accordingly includes the case where the angle is greater than or equal to 85° and less than or equal to 95° . The term “substantially perpendicular” indicates that the angle formed between two straight lines is greater than or equal to 60° and less than or equal to 120° .

In this specification, trigonal and rhombohedral crystal systems are included in a hexagonal crystal system.

According to one embodiment of the disclosed invention, the concentration of impurities contained in the oxide semiconductor layer can be reduced. In accordance with one embodiment of the present invention, electrical characteristics of a semiconductor device or the like including an oxide semiconductor can be improved. In accordance with one embodiment of the present invention, the reliability of a semiconductor device or the like including an oxide semiconductor can be improved. In accordance with one embodiment of the present invention, a novel semiconductor device or the like can be provided. Note that the description of these effects does not disturb the existence of other effects. One embodiment of the present invention does not necessarily achieve all the objects listed above. Other effects will be apparent from and can be derived from the description of the specification, the drawings, the claims, and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIGS. 1A and 1B are a plan view and a cross-sectional view of a transistor of one embodiment of the present invention;

FIGS. 2A and 2B are a plan view and a cross-sectional view of a transistor of one embodiment of the present invention;

FIGS. 3A and 3B are a plan view and a cross-sectional view of a transistor of one embodiment of the present invention;

FIGS. 4A and 4B are a plan view and a cross-sectional view of a transistor of one embodiment of the present invention;

FIGS. 5A to 5D are cross-sectional views illustrating a manufacturing process of a transistor of one embodiment of the present invention;

FIGS. 6A to 6C are cross-sectional views illustrating a manufacturing process of a transistor of one embodiment of the present invention;

FIGS. 7A to 7C are a plan view, a cross-sectional view, and a band diagram of a transistor of one embodiment of the present invention;

FIGS. 8A to 8D are Cs-corrected high-resolution TEM images of a cross section of a CAAC-OS and a cross-sectional schematic view of the CAAC-OS;

FIGS. 9A and 9B show nanobeam electron diffraction patterns of oxide semiconductor films and FIGS. 9C and 9D illustrate an example of a transmission electron diffraction measurement apparatus;

FIG. 10A shows an example of structural analysis by transmission electron diffraction measurement and FIGS. 10B and 10C show plan-view TEM images;

FIGS. 11A to 11C show Id-Vg characteristics, a band diagram, and SIMS analysis results of a transistor;

FIGS. 12A and 12B show Id-Vg characteristics and a band diagram of a transistor;

FIGS. 13A to 13C show Id-Vg characteristics, a band diagram, and SIMS analysis results of a transistor;

FIGS. 14A to 14C show Id-Vg characteristics, a band diagram, and SIMS analysis results of a transistor;

FIGS. 15A to 15C show Id-Vg characteristics, a band diagram, and SIMS analysis results of a transistor;

FIG. 16 is a graph showing results of XRD measurement.

FIG. 17 is a band diagram;

FIGS. 18A to 18C are a block diagram and circuit diagrams illustrating a configuration of a display device of one embodiment of the present invention;

FIG. 19 illustrates a display module of one embodiment of the present invention;

FIGS. 20A to 20D are views illustrating electronic appliances according to embodiments of the present invention;

FIGS. 21A and 21B are a cross-sectional view and a band diagram of a transistor of one embodiment of the present invention;

FIGS. 22A to 22C are a plan view and cross-sectional views of a transistor of one embodiment of the present invention;

FIGS. 23A to 23D are Cs-corrected high-resolution TEM images of a plane of a CAAC-OS;

FIGS. 24A to 24C show structural analysis of a CAAC-OS and a single crystal oxide semiconductor by XRD;

FIGS. 25A and 25B show electron diffraction patterns of a CAAC-OS;

FIG. 26 shows a change of crystal parts of an In—Ga—Zn oxide owing to electron irradiation;

FIGS. 27A and 27B are schematic diagrams illustrating deposition models of a CAAC-OS and an nc-OS;

FIGS. 28A to 28C illustrate an InGaZnO₄ crystal and a pellet; and

FIGS. 29A to 29D are schematic diagrams illustrating a deposition model of a CAAC-OS.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the present invention will be described below in detail with reference to the drawings. Note that the present invention is not limited to the following description, and it is easily understood by those skilled in the art that the mode and details can be variously changed without departing from the spirit and scope of the present invention. Therefore, the present invention should not be interpreted as being limited to the description of Embodiments below. In addition, in the following embodiments, the same portions or portions having similar functions are denoted by the same reference numerals or the same hatching patterns in different drawings, and description thereof will not be repeated.

Note that in each drawing described in this specification, the size, the film thickness, or the region of each component may be exaggerated for clarity. Therefore, embodiments of the present invention are not limited to such a scale.

In this specification and the like, ordinal numbers such as “first”, “second”, and the like are used in order to avoid

confusion among components, and the terms do not limit the components numerically. Therefore, for example, description can be made even when “first” is replaced with “second” or “third”, as appropriate.

Functions of a “source” and a “drain” are sometimes interchanged with each other as appropriate when the direction of current flow is changed in circuit operation, for example. Thus, in this specification and the like, the terms “source” and “drain” can be replaced with each other.

Note that the term such as “over” or “below” in this specification and the like does not necessarily mean that a component is placed “directly on” or “directly under” another component. For example, the expression “a gate electrode layer over a gate insulating layer” does not exclude the case where a component is placed between the gate insulating layer and the gate electrode layer. The same applies to the term “below”.

In this specification, the term “parallel” indicates that the angle formed between two straight lines is greater than or equal to -10° and less than or equal to 100° , and accordingly also includes the case where the angle is greater than or equal to -5° and less than or equal to 5° . The term “perpendicular” indicates that the angle formed between two straight lines is greater than or equal to 80° and less than or equal to 100° , and accordingly includes the case where the angle is greater than or equal to 85° and less than or equal to 95° .

In this specification and the like, the trigonal and rhombohedral crystal systems are included in the hexagonal crystal system.

(Embodiment 1)

In this embodiment, a semiconductor device that is one embodiment of the present invention and a method for manufacturing the semiconductor device are described. Description is made with reference to FIGS. 1A and 1B, FIGS. 2A and 2B, FIGS. 3A and 3B, FIGS. 4A and 4B, FIGS. 5A to 5D, and FIGS. 6A to 6C.

<Structure Example 1 of Transistor>

FIGS. 1A to 1B are a plan view and a cross-sectional view of a transistor 200 included in a semiconductor device of this embodiment. The transistor 200 illustrated in FIGS. 1A and 1B is a channel-etched transistor. FIG. 1A is a plan view of the transistor 200, and FIG. 1B is a cross-sectional view taken along dashed dotted lines A1-A2 and B1-B2 in FIG. 1A. Note that a substrate 100 and some components (e.g., a gate insulating layer) of the transistor 200 are not illustrated in FIG. 1A for simplicity.

The transistor 200 illustrated in FIGS. 1A and 1B includes a gate electrode layer 102 formed over the substrate 100, a gate insulating layer 104 in contact with the gate electrode layer 102, an oxide semiconductor layer 106 facing the gate electrode layer 102 with the gate insulating layer 104 positioned therebetween, a metal oxide layer 108 over the oxide semiconductor layer 106, and a pair of electrode layers 110a and 110b in contact with the metal oxide layer 108. Furthermore, the transistor 200 may include an oxide insulating layer 112, an oxide insulating layer 114 and a nitride insulating layer 116 formed over the pair of electrode layers 110a and 110b and the metal oxide layer 108.

In the transistor 200, the metal oxide layer 108, which is provided in contact with the top surface of the oxide semiconductor layer 106 where a channel is formed, functions as a barrier layer for preventing diffusion of constituent elements of the pair of electrode layers 110a and 110b into the oxide semiconductor layer 106. In addition, the metal oxide layer 108 can also prevent constituent elements of the oxide insulating layer 112 or the like provided over the oxide semiconductor layer 106 from mixing into the oxide semiconductor

layer 106. The prevention of mixing of impurities into the oxide semiconductor layer 106 where the channel is formed can inhibit a reduction in the electrical characteristics of the transistor 200.

For the metal oxide layer 108, a metal oxide represented as In-M oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) can be used. Note that to prevent the metal oxide layer 108 from functioning as part of a channel formation region, a material having sufficiently low conductivity is used. Alternatively, for the metal oxide layer 108, a material which has smaller electron affinity (energy difference between the vacuum level and the bottom of the conduction band) than the oxide semiconductor layer 106 and has a difference in energy of the bottom of the conduction band from the oxide semiconductor layer 106 (i.e., has a band offset) is used. To prevent generation of a difference in threshold voltage depending on the level of a drain voltage, the material of the metal oxide layer 108 is preferably selected so that the energy of the bottom of the conduction band of the metal oxide layer 108 is closer to the vacuum level than the energy of the bottom of the conduction band of the oxide semiconductor layer 106 by 0.2 eV or more, preferably 0.5 eV or more.

In addition, increasing the atomic ratio of the element M to In can increase the energy gap of the metal oxide layer 108 and reduce the electron affinity. Accordingly, to prevent formation of a channel in the metal oxide layer 108 by forming the band offset of the conduction band between the metal oxide layer 108 and the oxide semiconductor layer 106, $y/(x+y)$ is preferably greater than or equal to 0.75 and less than 1, further preferably greater than or equal to 0.78 and less than 1, still further preferably greater than or equal to 0.80 and less than 1 where the atomic ratio of In to M included in the metal oxide layer is In:M=x:y. Note that, an element that is not indium, M, nor oxygen, which are main components of the metal oxide layer 108, may be mixed to the metal oxide layer 108 as an impurity. The concentration of the impurity in this case is preferably less than or equal to 0.1%. The atomic ratio of In:M=x:y can be measured by inductively coupled plasma mass spectrometry (ICP-MS). In:M=x:y refers to not the composition of the target but the composition of the metal oxide film obtained by a sputtering method, and $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where the atomic ratio is In:M=x:y.

In the case where the metal oxide layer 108 is formed by a sputtering method, when the atomic ratio of the element M to In is increased, the number of particles in deposition can be reduced. To reduce the number of particles, $y/(x+y)$ may be greater than or equal to 0.90, e.g., 0.93 where the atomic ratio is In:M=x:y. Note that in the case where the metal oxide layer 108 is formed by a sputtering method, when the atomic ratio of M to In is too high, the insulating property of a target becomes high, which makes it difficult to perform deposition using DC discharge; as a result, it is necessary to use RF discharge. Accordingly, when deposition is performed using DC discharge, which is applicable to the case of using a large-sized substrate, $y/(x+y)$ is set less than or equal to 0.96, preferably less than or equal to 0.95, e.g., 0.93. The use of the deposition method applicable to the case of using a large-sized substrate can increase the productivity of the semiconductor device.

Note that in the transistor 200, side surfaces of the oxide semiconductor layer 106 where the channel is formed are in contact with the pair of electrode layers 110a and 110b functioning as a source electrode layer and a drain electrode layer, and in the contact regions, a source region and a drain region are formed. Therefore, the metal oxide layer 108 may have an insulating property.

Note that it is preferable that the metal oxide layer **108** not have a spinel crystal structure. This is because if the metal oxide layer **108** has a spinel crystal structure, a constituent element of the pair of electrode layers **110a** and **110b** might be diffused into the oxide semiconductor layer **106** owing to the spinel crystal structure. For example, it is preferable that an In-M oxide be used as the metal oxide layer **108** and that a divalent metal element (e.g., zinc) not be contained as M, in which case the formed metal oxide layer **108** does not have a spinel crystal structure.

The thickness of the metal oxide layer **108** is greater than or equal to a thickness that is capable of inhibiting diffusion of the constituent element of the pair of electrode layers **110a** and **110b** into the oxide semiconductor layer **106**, and less than a thickness which inhibits supply of oxygen from the oxide insulating layer **112** to the oxide semiconductor layer **106**. For example, when the thickness of the metal oxide layer **108** is greater than or equal to 10 nm, the constituent element of the pair of electrode layers **110a** and **110b** can be prevented from diffusing into the oxide semiconductor layer **106**. When the thickness of the metal oxide layer **108** is less than or equal to 100 nm, oxygen can be effectively supplied from the oxide insulating layers **112** and **114** to the oxide semiconductor layer **106**.

In the transistor **200** described in this embodiment, the pair of electrode layers **110a** and **110b** functioning as source and drain electrode layers are preferably formed with a single layer or a stacked layer of a single metal that is a low-resistance material, such as copper, aluminum, gold, or silver; an alloy containing any of these materials, or a compound containing any of these materials as a main component. The pair of electrode layers **110a** and **110b** also functions as wirings; therefore, even in the case where a large-sized substrate is used as the substrate **100**, when the electrode layers are formed to contain a low-resistance material such as copper, aluminum, gold, or silver, a semiconductor device in which wiring delay is suppressed can be manufactured.

In the case where the pair of electrode layers **110a** and **110b** has a two-layer structure, the pair of electrode layers **110a** and **110b** is formed so that the second conductive layer is thick and contains a single metal that is a low-resistance material, such as copper, aluminum, gold, or silver, an alloy containing any of these materials, or a compound containing any of these components as a main component; and a conductor functioning as a barrier layer against a conductor of the second conductive layer is used for the first conductive layer that is in contact with the side surface of the oxide semiconductor layer **106** and the side surface and top surface of the metal oxide layer **108**. For example, a conductive layer of titanium, tantalum, molybdenum, tungsten; an alloy containing any of these elements; or a conductive layer containing titanium nitride, tantalum nitride, molybdenum nitride, tungsten nitride; or the like can be used as the barrier layer. In the case where the pair of electrode layers **110a** and **110b** has a three-layer structure, the third conductive layer is preferably formed using a conductor functioning as a barrier layer against a conductor of the second conductive layer so as to be over and in contact with the first and second conductive layers.

In the case where the pair of electrode layers **110a** and **110b** has a two-layer structure, for example, any of the following structures is preferably used: a structure in which an aluminum film is stacked on a titanium film; a structure in which a copper film is stacked on a tungsten film; a structure in which an aluminum film is stacked on a tungsten film; a structure in which a copper film is stacked on a copper-magnesium-aluminum alloy film; a structure in which a copper film is stacked

on a titanium film; and a structure in which a copper film is stacked on a tungsten film. In the case where the pair of electrode layers **110a** and **110b** has three-layer structure, a film formed of titanium, titanium nitride, molybdenum, or molybdenum nitride is preferably formed as each of the first and third conductive layers, and a film formed of a low-resistance material such as copper, aluminum, gold, or silver is preferably formed as the second conductive layer.

The pair of electrode layers functioning as source and drain electrode layers in the transistor **200** described in this embodiment is formed using electrode layers including a low-resistance material such as copper, aluminum, gold, or silver, whereby the semiconductor device in which wiring delay is suppressed can be manufactured. Furthermore, the metal oxide layer **108** functioning as a barrier layer is provided in contact with the pair of electrode layers, whereby a reduction in electrical characteristics can be prevented, and thus it is possible to provide a semiconductor device having favorable electrical characteristics.

Note that the number of masks may be reduced by forming the electrode layers **110a** and **110b**, the oxide semiconductor layer **106**, and the metal oxide layer **108** with the use of a half-tone mask (or a gray-tone mask, a phase difference mask, or the like), so that the number of processing steps may be reduced. In this case, a pattern is formed by, for example, ashing of a resist. Therefore, the oxide semiconductor layer **106** and the metal oxide layer **108** are necessarily provided below the electrode layers **110a** and **110b**. FIGS. **22A** to **22C** are a plan view and cross-sectional views of the structure in FIGS. **1A** and **1B** in the case where a half-tone mask is used.

Other constituent elements of the semiconductor device of this embodiment are described below in detail.
(Substrate)

There is no particular limitation on a material or the like of the substrate **100** as long as the material has heat resistance enough to withstand at least heat treatment to be performed later. For example, a glass substrate, a ceramic substrate, a quartz substrate, or a sapphire substrate may be used as the substrate **100**. Alternatively, a single crystal semiconductor substrate or a polycrystalline semiconductor substrate made of silicon, silicon carbide, or the like, a compound semiconductor substrate made of silicon germanium or the like, an SOI (silicon on insulator) substrate, or the like may be used as the substrate **400**. Furthermore, any of these substrates further provided with a semiconductor element may be used as the substrate **100**. In the case where a glass substrate is used as the substrate **100**, a glass substrate having any of the following sizes can be used: the 6th generation (1500 mm×1850 mm), the 7th generation (1870 mm×2200 mm), the 8th generation (2200 mm×2400 mm), the 9th generation (2400 mm×2800 mm), and the 10th generation (2950 mm×3400 mm). Thus, a large-sized display device can be manufactured.

Further alternatively, a flexible substrate may be used as the substrate **100**, and the transistor **200** may be provided directly on the flexible substrate. Alternatively, a separation layer may be provided between the substrate **100** and the transistor **200**. The separation layer can be used when part or the whole of a semiconductor device formed over the separation layer is separated from the substrate **100** and transferred onto another substrate. In that case, the transistor **200** can be transferred to a substrate having low heat resistance or a flexible substrate.
(Gate Electrode Layer)

The gate electrode layer **102** can be formed using a metal element selected from chromium, copper, aluminum, gold, silver, zinc, molybdenum, tantalum, titanium, and tungsten; an alloy containing any of these metal elements as a component; an alloy containing any of these metal elements in

combination; or the like. Further, one or more metal elements selected from manganese and zirconium may be used. Furthermore, the gate electrode layer **102** may have a single-layer structure or a stacked-layer structure of two or more layers. For example, a single-layer structure of an aluminum film containing silicon, a two-layer structure in which a titanium film is stacked over an aluminum film, a two-layer structure in which a titanium film is stacked over a titanium nitride film, a two-layer structure in which a tungsten film is stacked over a titanium nitride film, a two-layer structure in which a tungsten film is stacked over a tantalum nitride film or a tungsten nitride film, a three-layer structure in which a titanium film, an aluminum film, and a titanium film are stacked in this order, and the like can be given. Alternatively, an alloy film or a nitride film which contains aluminum and one or more elements selected from titanium, tantalum, tungsten, molybdenum, chromium, neodymium, and scandium may be used.

The gate electrode layer **102** can also be formed using a light-transmitting conductive material such as indium tin oxide, indium oxide containing tungsten oxide, indium zinc oxide containing tungsten oxide, indium oxide containing titanium oxide, indium tin oxide containing titanium oxide, indium zinc oxide, or indium tin oxide to which silicon oxide is added. It is also possible to have a stacked-layer structure formed using the above light-transmitting conductive material and the above metal element.

Further, an In—Ga—Zn-based oxynitride semiconductor film, an In—Sn-based oxynitride semiconductor film, an In—Ga-based oxynitride semiconductor film, an In—Zn-based oxynitride semiconductor film, a Sn-based oxynitride semiconductor film, an In-based oxynitride semiconductor film, a film of metal nitride (such as InN or ZnN), or the like may be provided between the gate electrode layer **102** and the gate insulating layer **104**. These films each have a work function of 5 eV or higher, preferably 5.5 eV or higher, which is higher than the electron affinity of an oxide semiconductor, thus, the threshold voltage of a transistor including the oxide semiconductor can be shifted in the positive direction. Accordingly, a switching element having what is called normally-off characteristics is obtained. For example, in the case of using an In—Ga—Zn-based oxynitride semiconductor film, an In—Ga—Zn-based oxynitride semiconductor film having a higher nitrogen concentration than at least the oxide semiconductor layer **106**, specifically, an In—Ga—Zn-based oxynitride semiconductor film having a nitrogen concentration of 7 atomic % or higher is used.

(Gate Insulating Layer)

The gate insulating layer **104** can be formed to have a single-layer structure or a stacked-layer structure using, for example, one or more of silicon oxide, silicon oxynitride, silicon nitride oxide, silicon nitride, aluminum oxide, hafnium oxide, gallium oxide, and Ga—Zn-based metal oxide.

Alternatively, the gate insulating layer **104** may be formed using a high-k material such as hafnium silicate (HfSiO_x), hafnium silicate to which nitrogen is added ($\text{HfSi}_x\text{O}_y\text{N}_z$), hafnium aluminate to which nitrogen is added ($\text{HfAl}_x\text{O}_y\text{N}_z$), hafnium oxide, or yttrium oxide, in which case gate leakage current of the transistor can be reduced.

The thickness of the gate insulating layer **104** is greater than or equal to 5 nm and less than or equal to 400 nm, preferably greater than or equal to 10 nm and less than or equal to 300 nm, more preferably greater than or equal to 50 nm and less than or equal to 250 nm.

(Oxide Semiconductor Layer)

The oxide semiconductor layer **106** is typically formed using an In—Ga oxide, an In—Zn oxide, or an In—M—Zn oxide (M is Al, Ti, Ga, Y, Zr, La, Ce, Nd, or Hf).

In the case where the oxide semiconductor layer **106** is an In—M—Zn oxide (M is Al, Ti, Ga, Y, Zr, La, Ce, Nd, or Hf), it is preferable that the atomic ratio of metal elements of a sputtering target used for forming a film of the In—M—Zn oxide satisfy $\text{In} \geq \text{M}$ and $\text{Zn} \geq \text{M}$. As the atomic ratio of metal elements of such a sputtering target, In:M:Zn=1:1:1, In:M:Zn=1:1:1.2, and In:M:Zn=3:1:2 are preferable. Note that the atomic ratio of metal elements in the formed oxide semiconductor layer **106** varies from the above atomic ratio of metal elements of the sputtering target within a range of $\pm 40\%$ as an error.

In the case of using an In—M—Zn oxide for the oxide semiconductor layer **106**, when Zn and O are eliminated from consideration, the atomic percentage of In and the atomic percentage of M are preferably greater than 25 atomic % and less than 75 atomic %, respectively, further preferably greater than 34 atomic % and less than 66 atomic %, respectively.

The energy gap of the oxide semiconductor layer **106** is 2 eV or more, preferably 2.5 eV or more, further preferably 3 eV or more. With the use of an oxide semiconductor having such a wide energy gap, the off-state current of the transistor **200** can be reduced.

The thickness of the oxide semiconductor layer **106** is greater than or equal to 3 nm and less than or equal to 200 nm, preferably greater than or equal to 3 nm and less than or equal to 100 nm, further preferably greater than or equal to 3 nm and less than or equal to 50 nm.

An oxide semiconductor layer with low carrier density is used as the oxide semiconductor layer **106**. For example, an oxide semiconductor layer whose carrier density is lower than or equal to $1 \times 10^{17}/\text{cm}^3$, preferably lower than or equal to $1 \times 10^{15}/\text{cm}^3$, further preferably lower than or equal to $1 \times 10^{13}/\text{cm}^3$, still further preferably lower than or equal to $1 \times 10^{11}/\text{cm}^3$ is used as the oxide semiconductor layer **106**.

Note that, without limitation to the compositions and materials described above, a material with an appropriate composition may be used depending on required semiconductor characteristics and electrical characteristics (e.g., field-effect mobility and threshold voltage) of a transistor. Furthermore, in order to obtain the required semiconductor characteristics of the transistor, it is preferable that the carrier density, the impurity concentration, the defect density, the atomic ratio of a metal element to oxygen, the interatomic distance, the density, and the like of the oxide semiconductor layer **106** be set to appropriate values.

Note that it is preferable to use, as the oxide semiconductor layer **106**, an oxide semiconductor layer in which the impurity concentration is low and the density of defect states is low, in which case the transistor can have more excellent electrical characteristics. Here, the state in which impurity concentration is low and density of defect states is low (the number of oxygen vacancies is small) is referred to as “highly purified intrinsic” or “highly purified substantially intrinsic”. A highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor has few carrier generation sources, and thus can have a low carrier density. Thus, a transistor including the oxide semiconductor layer in which a channel region is formed rarely has a negative threshold voltage (is rarely normally-on). Thus, the transistor including the oxide semiconductor layer in the channel formation region has a small variation in electrical characteristics and high reliability in some cases. Furthermore, the highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor

layer has an extremely low off-state current; even when an element has a channel width of $1 \times 10^6 \mu\text{m}$ and a channel length L of $10 \mu\text{m}$, the off-state current can be less than or equal to the measurement limit of a semiconductor parameter analyzer, i.e., less than or equal to 1×10^{-13} A, at a voltage (drain voltage) between a source electrode and a drain electrode in the range from 1 V to 10 V.

Thus, the transistor in which the channel region is formed in the highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor layer can have a small variation in electrical characteristics and high reliability. Charges trapped by the trap states in the oxide semiconductor film take a long time to be released and may behave like fixed charges. Thus, the transistor in which the channel region is formed in the oxide semiconductor layer having a high density of defect states may have unstable electrical characteristics. As examples of the impurities, hydrogen, nitrogen, alkali metal, alkaline earth metal, and the like are given.

Hydrogen contained in the oxide semiconductor layer reacts with oxygen bonded to a metal atom to be water, and also causes oxygen vacancy in a lattice from which oxygen is released (or a portion from which oxygen is released). Due to entry of hydrogen into the oxygen vacancy, an electron serving as a carrier is generated. Furthermore, in some cases, bonding of part of hydrogen to oxygen bonded to a metal element causes generation of an electron serving as a carrier. Thus, a transistor including an oxide semiconductor which contains hydrogen is likely to be normally on. Accordingly, it is preferable that hydrogen be reduced as much as possible in the oxide semiconductor layer **106**. Specifically, in the oxide semiconductor layer **106**, the concentration of hydrogen which is measured by secondary ion mass spectrometry (SIMS) is lower than or equal to 2×10^{20} atoms/cm³, preferably lower than or equal to 5×10^{19} atoms/cm³, further preferably lower than or equal to 1×10^{19} atoms/cm³, or lower than 5×10^{18} atoms/cm³, preferably lower than or equal to 1×10^{18} atoms/cm³, further preferably lower than or equal to 5×10^{17} atoms/cm³, still further preferably lower than or equal to 1×10^{16} atoms/cm³.

When silicon or carbon which is one of elements belonging to Group 14 is contained in the oxide semiconductor layer **106**, the amount of oxygen vacancy is increased, and the oxide semiconductor layer **106** is changed to an n-type. Thus, the concentration of silicon or carbon (the concentration is measured by SIMS) in the oxide semiconductor layer **106** or the concentration of silicon or carbon (the concentration is measured by SIMS) in the vicinity of the interface between the metal oxide layer **108** and the oxide semiconductor layer **106** is set to be lower than or equal to 2×10^{18} atoms/cm³, preferably lower than or equal to 2×10^{17} atoms/cm³.

Furthermore, the concentration of alkali metal or alkaline earth metal of the oxide semiconductor layer **106**, which is measured by SIMS, is lower than or equal to 1×10^{18} atoms/cm³, preferably lower than or equal to 2×10^{16} atoms/cm³. Alkali metal and alkaline earth metal might generate carriers when bonded to an oxide semiconductor, in which case the off-state current of the transistor might be increased. Therefore, it is preferable to reduce the concentration of alkali metal or alkaline earth metal of the oxide semiconductor layer **106**.

In addition, when nitrogen is contained in the oxide semiconductor layer **106**, electrons serving as carriers are generated to increase the carrier density, so that the oxide semiconductor layer **106** easily becomes n-type. Thus, a transistor including an oxide semiconductor which contains nitrogen is likely to be normally on. For this reason, nitrogen in the oxide semiconductor film is preferably reduced as much as possible;

the concentration of nitrogen which is measured by SIMS is preferably set to, for example, lower than or equal to 5×10^{18} atoms/cm³.

The oxide semiconductor layer **106** may have a non-single crystal structure, for example. The non-single crystal structure includes a c-axis aligned crystalline oxide semiconductor (CAAC-OS) which is described later, a polycrystalline structure, a microcrystalline structure described later, or an amorphous structure, for example. Among the non-single crystal structure, the amorphous structure has the highest density of defect levels, whereas CAAC-OS has the lowest density of defect levels.

The oxide semiconductor layer **106** may have an amorphous structure, for example. The oxide semiconductor film having the amorphous structure has disordered atomic arrangement and no crystalline component, for example. Alternatively, the oxide film having an amorphous structure has, for example, an absolutely amorphous structure and no crystal part.

Note that the oxide semiconductor layer **106** may be a mixed film including two or more of the following: a region having an amorphous structure, a region having a microcrystalline structure, a region having a polycrystalline structure, a region of CAAC-OS described later, and a region having a single-crystal structure. The mixed film includes, for example, two or more of a region having an amorphous structure, a region having a microcrystalline structure, a region having a polycrystalline structure, a CAAC-OS region, and a region having a single-crystal structure in some cases. Further, the mixed film has a stacked-layer structure of two or more of a region having an amorphous structure, a region having a microcrystalline structure, a region having a polycrystalline structure, a CAAC-OS region, and a region having a single-crystal structure in some cases. Note that the metal oxide layer **108** in contact with the oxide semiconductor layer **106** can have an amorphous structure, a microcrystalline structure, a polycrystalline structure, or the like, for example.

In the case where an insulating layer which contains a different constituent element (e.g., silicon) from the oxide semiconductor is provided in contact with the oxide semiconductor layer **106**, an interface state due to heterojunction, entry of impurities, or the like might be formed at the interface between the oxide semiconductor layer **106** and the insulating layer. In the transistor **200** of this embodiment, the metal oxide layer **108** which has the same constituent element as the oxide semiconductor is provided between the oxide semiconductor layer **106** and the oxide insulating layer **112** which may have a different constituent element (e.g., silicon) from the oxide semiconductor. Hence, if trap states are formed between the metal oxide layer **108** and the oxide insulating layer **112** owing to impurities and defects, electrons flowing in the oxide semiconductor layer **106** are less likely to be captured by the trap states because there is a distance between the trap states and the oxide semiconductor layer **106**. Accordingly, the amount of on-state current of the transistor can be increased, and the field-effect mobility can be increased. When the electrons are captured by the trap states, the electrons become negative fixed charges. As a result, the threshold voltage of the transistor fluctuates. However, by the distance between the oxide semiconductor layer **106** and the trap states, capture of the electrons by the trap states can be reduced, and accordingly a fluctuation of the threshold voltage can be reduced.

The element M contained in the metal oxide layer **108** has a high bonding strength to oxygen; therefore, oxygen vacancy is less likely to be formed in the metal oxide layer **108** in which the atomic ratio of the element M is high. Therefore, it is

13

possible to reduce the amount of oxygen vacancy in the oxide semiconductor layer **106** in contact with the metal oxide layer **108**.

(Oxide Insulating Layer)

The oxide insulating layer **112** is an oxide insulating film through which oxygen is passed. Note that the oxide insulating layer **112** also functions as a film which relieves damage to the metal oxide layer **108** and the oxide semiconductor layer **106** when the oxide insulating layer **114** formed later is formed.

A silicon oxide film, a silicon oxynitride film, or the like with a thickness greater than or equal to 5 nm and less than or equal to 150 nm, preferably greater than or equal to 5 nm and less than or equal to 50 nm can be used as the oxide insulating layer **112**. Note that in this specification, "silicon oxynitride film" refers to a film that contains more oxygen than nitrogen, and "silicon nitride oxide film" refers to a film that contains more nitrogen than oxygen.

In addition, it is preferable that the number of defects in the oxide insulating layer **112** be small and typically, the spin density of a signal that appears at $g=2.001$ due to a dangling bond of silicon be lower than or equal to 3×10^{17} spins/cm³ by electron spin resonance (ESR) measurement. This is because if the density of defects in the oxide insulating layer **112** is high, oxygen is bonded to the defects and the amount of oxygen that passes through the oxide insulating layer **112** is decreased.

Moreover, it is preferable that the amount of defects at the interface between the oxide insulating layer **112** and the metal oxide layer **108** be small, typically the spin density corresponding to a signal which appears at g of greater than or equal to 1.89 and less than or equal to 1.93 due to an oxygen vacancy in the metal oxide layer **108** be lower than or equal to 1×10^{17} spins/cm³, more preferably lower than or equal to the lower limit of detection by ESR measurement.

Note that all oxygen entering the oxide insulating layer **112** from the outside does not move to the outside of the oxide insulating layer **112** and some oxygen remains in the oxide insulating layer **112**. Furthermore, movement of oxygen occurs in the oxide insulating layer **112** in some cases in such a manner that oxygen enters the oxide insulating layer **112** and oxygen contained in the oxide insulating layer **112** moves to the outside of the oxide insulating layer **112**. When an oxide insulating film which is permeable to oxygen is formed as the oxide insulating layer **112**, oxygen released from the oxide insulating layer **114** provided over the oxide insulating layer **112** can be moved to the oxide semiconductor layer **106** through the oxide insulating layer **112**.

The oxide insulating layer **114** is formed in contact with the oxide insulating layer **112**. The oxide insulating layer **114** is formed using an oxide insulating film whose oxygen content is in excess of that in the stoichiometric composition. Part of oxygen is released by heating from the oxide insulating film containing more oxygen than that in the stoichiometric composition. The oxide insulating film containing more oxygen than that in the stoichiometric composition is an oxide insulating film of which the amount of released oxygen converted into oxygen atoms is greater than or equal to 1.0×10^{18} atoms/cm³, preferably greater than or equal to 3.0×10^{20} atoms/cm³ in TDS analysis. Note that the substrate temperature in the TDS analysis is preferably higher than or equal to 100° C. and lower than or equal to 700° C., or higher than or equal to 100° C. and lower than or equal to 500° C.

A silicon oxide film, a silicon oxynitride film, or the like with a thickness greater than or equal to 30 nm and less than

14

or equal to 500 nm, preferably greater than or equal to 50 nm and less than or equal to 400 nm can be used for the oxide insulating layer **114**.

It is preferable that the amount of defects in the oxide insulating layer **114** be small, and typically the spin density corresponding to a signal which appears at $g=2.001$ due to a dangling bond of silicon, be lower than 1.5×10^{18} spins/cm³, more preferably lower than or equal to 1×10^{18} spins/cm³ by ESR measurement. Note that the oxide insulating layer **114** is provided more apart from the oxide semiconductor layer **106** than the oxide insulating layer **112** is; thus, the oxide insulating layer **114** may have higher defect density than the oxide insulating layer **112**.

(Nitride Insulating Layer)

It is possible to prevent outward diffusion of oxygen from the oxide semiconductor layer **106** and entry of hydrogen, water, and the like into the oxide semiconductor layer **106** from the outside by providing the nitride insulating layer **116** having a blocking effect against oxygen, hydrogen, water, alkali metal, alkaline earth metal, and the like over the oxide insulating layer **114**. The nitride insulating layer is formed using silicon nitride, silicon nitride oxide, aluminum nitride, aluminum nitride oxide, or the like. Note that instead of the nitride insulating layer having a blocking effect against oxygen, hydrogen, water, alkali metal, alkaline earth metal, and the like, an oxide insulating layer having a blocking effect against oxygen, hydrogen, water, and the like, may be provided. As the oxide insulating layer having a blocking effect against oxygen, hydrogen, water, and the like, aluminum oxide, aluminum oxynitride, gallium oxide, gallium oxynitride, yttrium oxide, yttrium oxynitride, hafnium oxide, and hafnium oxynitride can be given.

<Structure Example 2 of Transistor>

FIGS. 2A to 2B are a plan view and a cross-sectional view of a transistor **210** included in a semiconductor device of this embodiment. FIG. 2A is a plan view of the transistor **210**, and FIG. 2B is a cross-sectional view taken along dashed dotted lines A3-A4 and B3-B4 in FIG. 2A. Note that the substrate **100** and some components (e.g., a gate insulating layer) of the transistor **210** are not illustrated in FIG. 2A for simplicity.

The transistor **210** illustrated in FIGS. 2A and 2B includes the gate electrode layer **102** formed over the substrate **100**; the gate insulating layer **104** in contact with the gate electrode layer **102**; an oxide semiconductor layer **206** facing the gate electrode layer **102** with the gate insulating layer **104** positioned therebetween; the metal oxide layer **108** over the oxide semiconductor layer **206**; the pair of electrode layers **110a** and **110b** in contact with the metal oxide layer **108**; the oxide insulating layer **112**, the oxide insulating layer **114**, and the nitride insulating layer **116** formed over the pair of electrode layers **110a** and **110b** and the metal oxide layer **108**; and an electrode layer **118** formed over the nitride insulating layer **116**.

The electrode layer **118** functions as a back gate electrode in the transistor **210**. A stacked-layer structure that includes the oxide insulating layer **112**, the oxide insulating layer **114**, and the nitride insulating layer **116** and is provided between the electrode layer **118** and the oxide semiconductor layer **206** functions as a gate insulating layer for the back gate electrode. The electrode layer **118** is connected to the gate electrode layer **102** through opening portions **117a** and **117b** formed in the gate insulating layer **104**, the oxide insulating layer **112**, the oxide insulating layer **114**, and the nitride insulating layer **116**. Therefore, the same potential is applied to the electrode layer **118** and the gate electrode layer **102**.

The transistor **210** in FIGS. 2A and 2B is different from the transistor **200** in FIGS. 1A and 1B in that the electrode layer

15

118 functioning as a back gate electrode is provided over the nitride insulating layer 116. The other structures are the same as those of the transistor 200 and the effect similar to that in the case of the transistor 200 can be obtained. That is, the transistor 210 includes the metal oxide layer 108 which functions as a barrier layer and which is positioned between the pair of electrode layers 110a and 110b containing a low-resistance material and the oxide semiconductor layer 206 where a channel is formed. Thus, entry and diffusion of impurities to the oxide semiconductor layer 206 can be prevented. Thus, a reduction in the electrical characteristics is inhibited in the transistor 210. For details of every component in the transistor 210, the description of the transistor 200 can be referred to.

The oxide semiconductor layer 206 included in the transistor 210 in FIGS. 2A and 2B is formed using the same material as the oxide semiconductor layer 106 included in the transistor 200, and has a thickness greater than or equal to 100 nm, for example, greater than or equal to 100 nm and less than or equal to 1000 nm, preferably greater than or equal to 200 nm and less than or equal to 1000 nm. The channel length of the transistor 210 (the distance between the pair of electrode layers 110a and 110b) is preferably greater than or equal to 0.5 μm and less than or equal to 2 μm , further preferably greater than or equal to 0.5 μm and less than or equal to 1 μm .

As illustrated in the cross-sectional view of FIG. 2B, the oxide semiconductor layer 206 faces each of the gate electrode layer 102 and the electrode layer 118 (back gate electrode) to be positioned between the two electrode layers. The lengths in the channel length direction and the channel width direction of the electrode layer 118 functioning as a back gate electrode are longer than those of the oxide semiconductor layer 206, respectively. The whole oxide semiconductor layer 206 is covered with the electrode layer 118 with the insulating layers (the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116) positioned therebetween. Furthermore, since the electrode layer 118 and the gate electrode layer 102 are connected to each other through the opening portions 117a and 117b formed in the gate insulating layer 104, the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116, side surfaces of the oxide semiconductor layer 206 in the channel width direction face the back gate electrode (electrode layer 118) with the insulating layers (the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116) positioned therebetween.

Such a structure enables electric fields of the gate electrode layer 102 and the electrode layer 118 to electrically surround the oxide semiconductor layer 206 included in the transistor 210. A device structure of a transistor, like that of the transistor 210, in which electric fields of a gate electrode layer and a back gate electrode electrically surround an oxide semiconductor layer where a channel is formed can be referred to as a surrounded channel (s-channel) structure.

Since the transistor 210 has the s-channel structure, an electric field for inducing a channel can be effectively applied to the oxide semiconductor layer 206 by the gate electrode layer 102; therefore, the current drive capability of the transistor 210 can be improved and high on-state current characteristics can be obtained. Since the on-state current can be increased, it is possible to reduce the size of the transistor 210. Furthermore, since the transistor 210 has a structure in which the channel is surrounded by the gate electrode layer 102 and the electrode layer 118, the mechanical strength of the transistor 210 can be increased.

Note that in the structure of the transistor 210, any one of the opening portions 117a and 117b may be formed, and the

16

electrode layer 118 and the gate electrode layer 102 may be connected to each other through the opening portion.

Note that the pair of electrode layers 110a and 110b included in the transistor 210 has stacked-layer structures including first conductive layers 109a and 109b and second conductive layers 111a and 111b. Any of the materials given in the description of the first layer of the electrode layers 110a and 110b can be used for the first conductive layers 109a and 109b, as appropriate. In addition, any of the materials given in the description of the second layer of the electrode layers 110a and 110b can be used for the second conductive layers 111a and 111b, as appropriate. Note that the structure of the pair of electrode layers 110a and 110b of the transistor 210 is not limited to that illustrated in FIGS. 2A and 2B as long as the pair of the electrode layers 110a and 110b contain copper, aluminum, gold, or silver, and may be a single-layer structure or a stacked-layer structure of three layers or more.

<Structure Example 3 of Transistor>

FIGS. 3A to 3B are a plan view and a cross-sectional view of a transistor 220 included in a semiconductor device of this embodiment. The transistor 220 is a modification example of the transistor 210 in FIGS. 2A and 2B. FIG. 3A is a plan view of the transistor 220, and FIG. 3B is a cross-sectional view taken along dashed dotted lines A5-A6 and B5-B6 in FIG. 3A. Note that the substrate 100 and some components (e.g., a gate insulating layer) of the transistor 220 are not illustrated in FIG. 3A for simplicity.

The transistor 220 illustrated in FIGS. 3A and 3B includes the gate electrode layer 102 formed over the substrate 100; the gate insulating layer 104 in contact with the gate electrode layer 102; the oxide semiconductor layer 206 facing the gate electrode layer 102 with the gate insulating layer 104 positioned therebetween; the metal oxide layer 108 functioning as a barrier layer and provided over the oxide semiconductor layer 206; the pair of electrode layers 110a and 110b in contact with the metal oxide layer 108; the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116 formed over the pair of electrode layers 110a and 110b and the metal oxide layer 108; and electrode layers 119a, 119b, and 119c formed over the nitride insulating layer 116.

In the transistor 220, the electrode layer 119b, which overlaps the oxide semiconductor layer 206 with the metal oxide layer 108 and the insulating layers (the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116) positioned therebetween, functions as a back gate electrode. The electrode layers 119a and 119c, which are formed in the same layer as the electrode layer 119b, are connected to the gate electrode layer 102, through the opening portions 117a and 117b, respectively, which are formed in the gate insulating layer 104, the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116. That is, the electrode layers 119a and 119c function as part of the gate electrode layer 102.

The transistor 220 is different from the transistor 210 in that the electrode layer 118, which functions as a back gate electrode in the transistor 210, is separated. The other components of the transistor 220 can be similar to those of the transistor 210. The description of the transistor 210 can be referred to for details of the structure of the transistor 220.

The electrode layers 119a and 119c included in the transistor 220 have regions which overlap the oxide semiconductor layer 206 when seen from the above, and face the side surfaces of the oxide semiconductor layer 206 in the opening portions 117a and 117b. Thus, like the transistor 210, the transistor 220 also has an s-channel structure in which the oxide semiconductor layer 206 is electrically surrounded by

17

the gate electrode layer 102 and the electrode layers 119a, 119b, and 119c; therefore, an electric field for inducing a channel can be effectively applied to the oxide semiconductor layer 206 by the gate electrode layer 102. Accordingly, the current drive capability of the transistor 220 is increased, so that high on-state current can be obtained.

Furthermore, since the electrode layer 119b functioning as a back gate electrode is not electrically connected to the gate electrode layer 102 in the transistor 220, different potentials or signals can be input to the gate electrode layer 102 and the electrode layer 119b. Therefore, by a signal or potential input to the electrode layer 119b functioning as a back gate electrode, the threshold voltage of the transistor 220 can be shifted in the positive or negative direction. In the operation period of the semiconductor device, the transistor 220 can be changed to an enhancement-type or depression-type transistor, as appropriate by appropriate control of the threshold voltage of the transistor 220.

<Structure Example 4 of Transistor>

FIGS. 4A to 4B are a plan view and a cross-sectional view of a transistor 230 included in a semiconductor device of this embodiment. The transistor 230 is a modification example of the transistors 210 and 220 in FIGS. 2A and 2B and FIGS. 3A and 3B. FIG. 4A is a plan view of the transistor 230, and FIG. 4B is a cross-sectional view taken along dashed dotted lines A7-A8 and B7-B8 in FIG. 4A. Note that the substrate 100 and some components (e.g., a gate insulating layer) of the transistor 230 are not illustrated in FIG. 4A for simplicity.

The transistor 230 illustrated in FIGS. 4A and 4B includes the gate electrode layer 102 formed over the substrate 100; the gate insulating layer 104 in contact with the gate electrode layer 102; the oxide semiconductor layer 106 facing the gate electrode layer 102 with the gate insulating layer 104 positioned therebetween; the metal oxide layer 108 functioning as a barrier layer and provided over the oxide semiconductor layer 106; the pair of electrode layers 110a and 110b in contact with the metal oxide layer 108; the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116 formed over the pair of electrode layers 110a and 110b and the metal oxide layer 108; and the electrode layers 119a and 119c formed over the nitride insulating layer 116.

The transistor 230 includes the electrode layers 119a and 119c, which have regions overlapping the oxide semiconductor layer 106 with the metal oxide layer 108 and the insulating layers (the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116) positioned therebetween. The electrode layers 119a and 119c are connected to the gate electrode layer 102 through the opening portions 117a and 117b, respectively, which are formed in the gate insulating layer 104, the oxide insulating layer 112, the oxide insulating layer 114, and the nitride insulating layer 116, and the electrode layers 119a and 119c function as part of the gate electrode layer 102. That is, the transistor 230 has the structure of the transistor 220 in which the electrode layer 119b functioning as a back gate electrode is omitted. Note that only one of the electrode layers 119a and 119c may be provided in each of the transistor 220 and the transistor 230.

The transistor 230 also includes the gate electrode layers (the gate electrode layer 102 and the electrode layers 119a and 119c) that face the top and bottom surfaces and two facing side surfaces of the oxide semiconductor layer 206; therefore, like the transistors 210 and 220, the transistor 230 also has an s-channel structure in which the oxide semiconductor layer 206 is electrically surrounded. Therefore, the current drive capability of the transistor 230 is improved, so that the transistor 230 can have high on-state current. The descriptions of

18

the transistors 210 and 220 can be referred to for details of every components of the transistor 230.

Note that the structures of the transistors of this embodiment can be freely combined with each other.

<Method for Manufacturing Transistor>

A method for manufacturing the transistor of this embodiment is described using FIGS. 5A to 5D and FIGS. 6A to 6C. Note that a method for manufacturing the transistor 210 is described below as a typical example.

First, a conductive film is formed over the substrate 100 and processed through a photolithography process to form the gate electrode layer 102. Next, the gate insulating layer 104 is formed over the gate electrode layer 102 (see FIG. 5A).

The conductive film to be the gate electrode layer 102 can be formed by a sputtering method, a chemical vapor deposition (CVD) method, a vacuum evaporation method, or a pulsed laser deposition (PLD) method. Alternatively, a coating method or a printing method can be used. Although typical deposition methods are a sputtering method and a plasma chemical vapor deposition (PECVD) method, a thermal CVD method such as a metal organic chemical vapor deposition (MOCVD) method or an atomic layer deposition (ALD) method may be used.

A thermal CVD method is a deposition method in which deposition may be performed in such a manner that the pressure in a chamber is set to an atmospheric pressure or a reduced pressure, and a source gas and an oxidizer are supplied to the chamber at the same time and react with each other in the vicinity of the substrate or over the substrate to be deposited over the substrate. A thermal CVD method has an advantage that no defect due to plasma damage is generated since it does not utilize plasma for deposition.

Deposition by an ALD method may be performed in such a manner that the pressure in a chamber is set to an atmospheric pressure or a reduced pressure, source gases for reaction are sequentially introduced into the chamber, and then the sequence of the gas introduction is repeated. For example, two or more kinds of source gases are sequentially supplied to the chamber by switching respective switching valves (also referred to as high-speed valves). For example, a first source gas is introduced, an inert gas (e.g., argon or nitrogen) or the like is introduced at the same time as or after the introduction of the first gas so that the source gases are not mixed, and then a second source gas is introduced. Note that in the case where the first source gas and the inert gas are introduced at a time, the inert gas serves as a carrier gas, and the inert gas may also be introduced at the same time as the introduction of the second source gas. Alternatively, the first source gas may be exhausted by vacuum evacuation instead of the introduction of the inert gas, and then the second source gas may be introduced. The first source gas is adsorbed on the surface of the substrate to form a first single-atomic layer; then the second source gas is introduced to react with the first single-atomic layer; as a result, a second single-atomic layer is stacked over the first single-atomic layer, so that a thin film is formed. The sequence of the gas introduction is repeated plural times until a desired thickness is obtained, whereby a thin film with excellent step coverage can be formed. The thickness of the thin film can be adjusted by the number of repetition times of the sequence of the gas introduction; therefore, an ALD method makes it possible to accurately adjust a thickness and thus is suitable for manufacturing a minute FET.

In this embodiment, a glass substrate is used as the substrate 100, and a 100-nm-thick tungsten layer is formed as the gate electrode layer 102 by a sputtering method.

Note that for example, in the case where a tungsten layer is formed using a deposition apparatus utilizing ALD, a WF_6 gas and a B_2H_6 gas are sequentially introduced a plurality of times to form an initial tungsten layer, and then a WF_6 gas and an H_2 gas are introduced at a time, so that a tungsten layer is formed. Note that an SiH_4 gas may be used instead of a B_2H_6 gas.

The gate insulating layer **104** can be formed by a sputtering method, a PECVD method, a thermal CVD method, a vacuum evaporation method, a PLD method, or the like. Here, a stack including a 400-nm-thick silicon nitride film and a 50-nm-thick silicon oxynitride film is formed as the gate insulating layer **104** by a PECVD method.

Alternatively, a film to be the gate insulating layer **104** may be formed by a thermal CVD method. For example, in the case where a hafnium oxide film is formed, two kinds of gases, i.e., ozone (O_3) as an oxidizer and a source gas which is obtained by vaporizing liquid containing a solvent and a hafnium precursor compound (a hafnium alkoxide solution, typically tetrakis(dimethylamide)hafnium (TDMAH)) are used. Note that the chemical formula of tetrakis(dimethylamide)hafnium is $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$. Examples of another material liquid include tetrakis(ethylmethylamide)hafnium.

For example, in the case where an aluminum oxide film is formed, two kinds of gases, e.g., H_2O as an oxidizer and a source gas which is obtained by vaporizing liquid containing a solvent and an aluminum precursor compound (e.g. trimethylaluminum (TMA)) are used. Note that the chemical formula of trimethylaluminum is $\text{Al}(\text{CH}_3)_3$. Examples of another material liquid include tris(dimethylamide)aluminum, triisobutylaluminum, and aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate).

For example, in the case where a silicon oxide film is formed, hexachlorodisilane is adsorbed on a deposition surface, chlorine contained in the adsorbate is removed, and radicals of an oxidizing gas (e.g., O_2 or dinitrogen monoxide) are supplied to react with the adsorbate.

Next, a stack including an oxide semiconductor film **106a** to be the oxide semiconductor layer **106** and a metal oxide film **108a** to be the metal oxide layer **108** is formed over the gate insulating layer **104** (see FIG. 5B).

In this embodiment, an In—Ga—Zn oxide film is formed as the oxide semiconductor film **106a** by a sputtering method using an In—Ga—Zn oxide target (In:Ga:Zn=1:1:1). Furthermore, an In—Ga oxide film is formed as the metal oxide film **108a** by a sputtering method using an In—Ga oxide target (In:Ga=7:93). The metal oxide film **108a** is formed as an oxide semiconductor film or an insulating film. Note that the constituent elements and compositions applicable to the oxide semiconductor film **106a** and the metal oxide film **108a** are not limited thereto.

In the case where the oxide semiconductor film **106a** and the metal oxide film **108a** are formed by a sputtering method, a power supply device for generating plasma can be an RF power supply device, an AC power supply device, a DC power supply device, or the like as appropriate. Note that it is preferable to use DC discharge applicable to a large-sized substrate in deposition because the productivity of the semiconductor device can be increased. To deposit the metal oxide film **108a** by a sputtering method using DC discharge, it is preferable that $y/(x+y)$ be less than or equal to 0.96, further preferably less than or equal to 0.95, for example, 0.93 where an atomic ratio of In:M is x:y.

As a sputtering gas, a rare gas (typically argon), oxygen, or a mixed gas of a rare gas and oxygen is used as appropriate. In the case of using the mixed gas of a rare gas and oxygen, the proportion of oxygen to a rare gas is preferably increased.

A chamber in a sputtering apparatus is preferably evacuated to be a high vacuum state (to the degree of about 5×10^{-7} Pa to 1×10^{-4} Pa) with an adsorption vacuum evacuation pump such as a cryopump in order to remove water or the like, which serves as an impurity for the oxide semiconductor film **106a**, as much as possible. Alternatively, a turbo molecular pump and a cold trap are preferably combined so as to prevent a backflow of a gas, especially a gas containing carbon or hydrogen from an exhaust system to the inside of the chamber. It is preferable to remove impurities such as water contained in the metal oxide film **108a** in contact with the oxide semiconductor film **106a**, as much as possible; therefore, a chamber for depositing the metal oxide film **108a** is preferably evacuated to be a high vacuum state.

In order to obtain a highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor film, besides the high vacuum evacuation of the chamber, a highly purification of a sputtering gas is also needed. As an oxygen gas or an argon gas used for a sputtering gas, a gas which is highly purified to have a dew point of -40°C . or lower, -80°C . or lower, -100°C . or lower, or -120°C . or lower is used, whereby entry of moisture or the like into the oxide semiconductor film **106a** and the metal oxide film **108a** can be minimized.

Note that the oxide semiconductor film **106a** and/or the metal oxide film **108a** can be formed with a deposition apparatus utilizing ALD instead of sputtering. For example, in the case where an In—Ga—Zn oxide film is formed, an $\text{In}(\text{CH}_3)_3$ gas and an O_3 gas are sequentially introduced plural times to form an InO_2 layer, a $\text{Ga}(\text{CH}_3)_3$ gas and an O_3 gas are introduced at a time to form a GaO layer, and then a $\text{Zn}(\text{CH}_3)_2$ gas and an O_3 gas are introduced at a time to form a ZnO layer. Note that the order of these layers is not limited to this example. A mixed compound layer such as an InGaO_2 layer, an InZnO_2 layer, a GaInO layer, a ZnInO layer, or a GaZnO layer may be formed by mixing of these gases. Note that although an H_2O gas which is obtained by bubbling with an inert gas such as Ar may be used instead of an O_3 gas, it is preferable to use an O_3 gas, which does not contain H. Further, instead of an $\text{In}(\text{GH}_3)_3$ gas, an $\text{In}(\text{C}_2\text{H}_5)_3$ gas may be used. Instead of an $\text{In}(\text{CH}_3)_3$ gas, an $\text{In}(\text{C}_2\text{H}_5)_3$ may be used. Instead of a $\text{Ga}(\text{CH}_3)_3$ gas, a $\text{Ga}(\text{C}_2\text{H}_5)_3$ gas may be used. Furthermore, a $\text{Zn}(\text{CH}_3)_2$ gas may be used.

Next, a resist mask is formed over the metal oxide film **108a** through a photolithography process using a photoresist mask, and then the metal oxide film **108a** and the oxide semiconductor film **106a** are etched using the resist mask to be isolated for each element, so that the oxide semiconductor layer **106** and the metal oxide layer **108** are formed (see FIG. 5C). A wet etching method is preferably used for the etching. Note that a dry etching method may be used, or a combination of both methods may be used.

After the oxide semiconductor layer **106** is formed, heat treatment may be performed at a temperature higher than or equal to 150°C . and lower than the strain point of the substrate, preferably higher than or equal to 200°C . and lower than or equal to 450°C ., further preferably higher than or equal to 300°C . and lower than or equal to 450°C . The heat treatment performed here serves as one kind of treatment for increasing the purity of the oxide semiconductor layer and can reduce hydrogen, water, and the like contained in the oxide semiconductor layer **106**. Note that the heat treatment for the purpose of reducing hydrogen, water, and the like may be performed before the oxide semiconductor layer **106** is processed into an island shape. For example, the heat treatment may be performed in a period from deposition of the oxide semiconductor film **106a** to deposition of the metal

oxide film **108a**. In this case, the deposition temperature of the metal oxide film **108a** may be room temperature.

An electric furnace, an RTA apparatus, or the like can be used for the heat treatment performed on the oxide semiconductor layer **106**. With the use of an RTA apparatus, the heat treatment can be performed at a temperature higher than or equal to the strain point of the substrate if the heating time is short. Therefore, the heat treatment time can be shortened.

Note that the heat treatment performed on the oxide semiconductor layer **106** may be performed under an atmosphere of nitrogen, oxygen, ultra-dry air (air with a water content of 20 ppm or less, preferably 1 ppm or less, more preferably 10 ppb or less), or a rare gas (argon, helium, or the like). The atmosphere of nitrogen, oxygen, ultra-dry air, or a rare gas preferably does not contain hydrogen, water, and the like. Further, after heat treatment performed in a nitrogen atmosphere or a rare gas atmosphere, heat treatment may be additionally performed in an oxygen atmosphere or an ultra-dry air atmosphere. As a result, hydrogen, water, and the like can be released from the oxide semiconductor layer and oxygen can be supplied to the oxide semiconductor layer at the same time. Consequently, the amount of oxygen vacancies in the oxide semiconductor layer can be reduced.

Next, the pair of electrode layers **110a** and **110b** in contact with the side surfaces of the oxide semiconductor layer **106** and the side and top surfaces of the metal oxide layer **108** is formed (see FIG. 5D).

Here, a 50-nm-thick tungsten film to be the first conductive layers **109a** and **109b** and a 300-nm-thick copper film to be the second conductive layers **111a** and **111b** are formed by a sputtering method. Then, a resist mask is formed over the copper film through a photolithography process using a photoresist mask, and the tungsten film and the copper film are processed using the resist mask to be the pair of electrode layers **110a** and **110b**. Note that as described above, the conductive films such as the tungsten film and the copper film may be formed by an ALD method or a thermal CVD method. Any of these methods makes it possible to form the conductive films without plasma damage to the oxide semiconductor layer **106** and the metal oxide layer **108**.

For example, when a wet etching method is used for etching the copper film and a dry etching method using SF_6 is used for etching the tungsten film, a fluoride is formed on the surface of the copper film, and copper of the copper film can be prevented from diffusing to the oxide semiconductor layer **106** owing to the fluoride. In addition, the metal oxide layer **108** can function as an etching protective film for the oxide semiconductor layer **106**.

Then, the oxide insulating layer **112** is formed over the pair of electrode layers **110a** and **110b**. After that, the oxide insulating layer **114** is formed over the oxide insulating layer **112** (see FIG. 6A).

It is preferable to form the oxide insulating layer **114** without exposure to the atmosphere, directly after the oxide insulating layer **112** is formed. After the oxide insulating layer **112** is formed, the oxide insulating layer **114** is formed by adjusting at least one of the flow rate of a source gas, pressure, a high-frequency power, and a substrate temperature without exposure to the air, whereby the concentration of impurities attributed to the atmospheric component at the interface between the oxide insulating layer **112** and the oxide insulating layer **114** can be reduced and oxygen in the oxide insulating layer **114** can be moved to the oxide semiconductor layer **106**; accordingly, the amount of oxygen vacancy in the oxide semiconductor layer **106** can be reduced.

For example, a silicon oxide film or a silicon oxynitride film can be formed as the oxide insulating layer **112** under the

following conditions: the substrate placed in an evacuated treatment chamber of the plasma CVD apparatus is held at a temperature ranging from 180° C. to 400° C., preferably from 200° C. to 370° C.; the pressure of the chamber into which the source gas is introduced is set in the range from 20 Pa to 250 Pa, preferably from 100 Pa to 250 Pa; and high-frequency power is supplied to the electrode provided in the treatment chamber.

With the use of the above deposition conditions, an oxide insulating layer which is permeable to oxygen can be formed as the oxide insulating layer **112**. Further, by providing the metal oxide layer **108** and the oxide insulating layer **112**, damage to the oxide semiconductor layer **106** can be reduced in a step of forming the oxide insulating layer **114** which is formed later.

Under these deposition conditions, the bonding strength of silicon and oxygen becomes strong when the substrate temperature is higher than or equal to 300° C. and lower than or equal to 400° C., preferably higher than or equal to 320° C. and lower than or equal to 370° C. Thus, as the oxide insulating layer **112**, a dense and hard oxide insulating layer that is permeable to oxygen, typically, a silicon oxide film or a silicon oxynitride film of which etching using hydrofluoric acid of 0.5 wt % at 25° C. is performed at a rate of lower than or equal to 10 nm/min, preferably lower than or equal to 8 nm/min can be formed.

It is effective for release of hydrogen, water, and the like contained in the oxide semiconductor layer **106** and the metal oxide layer **108** in contact therewith to form the oxide insulating layer **112** while heating is performed in the step of depositing the oxide insulating layer **112**. Hydrogen contained in the oxide semiconductor layer **106** is bonded to an oxygen radical formed in plasma to form water. Since the substrate is heated in the step for depositing the oxide insulating layer **112**, water formed by bonding of oxygen and hydrogen is released from the oxide semiconductor layer **106**. That is, formation of the oxide insulating layer **112** by a plasma CVD method can reduce the amount of water, hydrogen, and the like contained in the oxide semiconductor layer **106**.

Furthermore, by setting the pressure in the treatment chamber to be higher than or equal to 100 Pa and lower than or equal to 250 Pa, the amount of water contained in the oxide insulating layer **112** is reduced; thus, variation in electrical characteristics of the transistor **210** can be reduced and change in threshold voltage can be inhibited.

Note that it is preferable to reduce damage to the oxide semiconductor layer **106** as much as possible at the time of depositing the oxide insulating layer **112**. This is because in the case where the oxide insulating layer **114** that is formed later for the purpose of improving the reliability of the transistor is formed under the conditions that can reduce the defects in the film, the amount of oxygen released from the oxide insulating layer **114** tends to be reduced, and thus it is difficult to adequately reduce defects of the oxide semiconductor layer **106**. Thus, it is preferable that the pressure in a treatment chamber be higher than or equal to 100 Pa and lower than or equal to 250 Pa at the time of depositing the oxide insulating layer **112**. Deposition under such conditions can reduce damage to the oxide semiconductor layer **106**.

Note that when the ratio of the amount of the oxidizing gas to the amount of the deposition gas containing silicon is 100 or higher, the hydrogen content in the oxide insulating layer **112** can be reduced. Consequently, the amount of hydrogen entering the oxide semiconductor layer **106** can be reduced, thereby inhibiting the negative shift in the threshold voltage of the transistor.

As the oxide insulating layer **114**, a silicon oxide film or a silicon oxynitride film is formed under the following conditions: the substrate placed in a treatment chamber of the plasma CVD apparatus that is vacuum-evacuated is held at a temperature higher than or equal to 180° C. and lower than or equal to 280° C., preferably higher than or equal to 200° C. and lower than or equal to 240° C. the pressure is greater than or equal to 100 Pa and less than or equal to 250 Pa, preferably greater than or equal to 100 Pa and less than or equal to 200 Pa with introduction of a source gas into the treatment chamber, and a high-frequency power of greater than or equal to 0.17 W/cm² and less than or equal to 0.5 W/cm², preferably greater than or equal to 0.25 W/cm² and less than or equal to 0.35 W/cm² is supplied to the electrode provided in the treatment chamber.

As the deposition conditions of the oxide insulating layer **114**, the high-frequency power having the above power density is supplied to the reaction chamber having the above pressure, whereby the degradation efficiency of the source gas in plasma is increased, oxygen radicals are increased, and oxidation of the source gas is promoted; therefore, the oxygen content of the oxide insulating layer **114** becomes higher than that in the stoichiometric composition. On the other hand, in the film formed at a substrate temperature within the above temperature range, a bond between silicon and oxygen is weak, and accordingly, part of oxygen in the film is released by heat treatment in a later step. Thus, it is possible to form an oxide insulating layer which contains oxygen in a proportion higher than that of oxygen in the stoichiometric composition and from which part of oxygen is released by heating.

Note that the oxide insulating layer **112** serves as a protective film of the metal oxide layer **108** in the step of forming the oxide insulating layer **114**. Furthermore, the metal oxide layer **108** serves as a protective film of the oxide semiconductor layer **106**. Consequently, the oxide insulating layer **114** can be formed using the high-frequency power having a high power density while damage to the oxide semiconductor layer **106** is reduced.

Note that in the deposition conditions of the oxide insulating layer **114**, when the flow rate of the deposition gas containing silicon with respect to the oxidizing gas is increased, the amount of defects in the oxide insulating layer **114** can be reduced. Typically, it is possible to form an oxide insulating layer in which the amount of defects is small, i.e., the spin density of a signal which appears at $g=2.001$ originating from a dangling bond of silicon is lower than 6×10^{17} spins/cm³, preferably lower than or equal to 3×10^{17} spins/cm³, further preferably lower than or equal to 1.5×10^{17} spins/cm³ by ESR measurement. As a result, the reliability of the transistor can be improved.

After the oxide insulating layers **112** and **114** are formed, heat treatment is performed. By the heat treatment, part of oxygen contained in the oxide insulating layer **114** can be moved to the oxide semiconductor layer **106**, so that the amount of oxygen vacancy contained in the oxide semiconductor layer **106** can be further reduced. After the heat treatment, the nitride insulating layer **116** is formed.

In the case where water, hydrogen, or the like is contained in the oxide insulating layers **112** and **114**, when the nitride insulating layer **116** having a function of blocking water, hydrogen, and the like is formed and then heat treatment is performed, water, hydrogen, or the like contained in the oxide insulating layers **112** and **114** are moved to the oxide semiconductor layer **106**, so that defects are generated in the oxide semiconductor layer **106**. Thus, when heat treatment is performed before formation of the nitride insulating layer **116**,

water or hydrogen contained in the oxide insulating layers **112** and **114** can be effectively reduced.

Note that when the oxide insulating layer **114** is formed over the oxide insulating layer **112** while being heated, oxygen can be moved to the oxide semiconductor layer **106** to reduce oxygen vacancy included in the oxide semiconductor layer **106**; therefore, the heat treatment is not necessarily performed in some cases.

The temperature of the heat treatment performed on the oxide insulating layers **112** and **114** is typically higher than or equal to 150° C. and lower than or equal to 400° C. preferably higher than or equal to 300° C. and lower than or equal to 400° C. further preferably higher than or equal to 320° C. and lower than or equal to 370° C. The heat treatment may be performed in an atmosphere of nitrogen, oxygen, ultra-dry air (air in which a water content is 20 ppm or less, preferably 1 ppm or less, further preferably 10 ppb or less), or a rare gas (argon, helium, or the like). Note that an electric furnace, an RTA apparatus, or the like can be used for the heat treatment, in which it is preferable that hydrogen, water, and the like not be contained in the nitrogen, oxygen, ultra-dry air, or rare gas.

Here, the heat treatment is performed at 350° C. in a mixed atmosphere of nitrogen and oxygen for one hour. After that, the nitride insulating layer **116** is formed (see FIG. 6A).

In the case where the nitride insulating layer **116** is formed by a plasma CVD method, the substrate temperature is preferably higher than or equal to 300° C. and lower than or equal to 400° C., further preferably higher than or equal to 320° C. and lower than or equal to 370° C. because a dense film can be formed.

For example, in the case where a silicon nitride film is formed as the nitride insulating layer **116** by the plasma CVD method, a deposition gas containing silicon, nitrogen, and ammonia are preferably used as a source gas. A small amount of ammonia compared to the amount of nitrogen is used, whereby ammonia is dissociated in plasma and activated species are generated. The activated species cleave a bond between silicon and hydrogen which are contained in a deposition gas containing silicon and a triple bond between nitrogen molecules. As a result, a dense silicon nitride film having few defects, in which bonds between silicon and nitrogen are promoted and bonds between silicon and hydrogen are few, can be formed. On the other hand, when the amount of ammonia with respect to nitrogen is large, decomposition of a deposition gas containing silicon and decomposition of nitrogen are not promoted, so that a sparse silicon nitride film in which bonds between silicon and hydrogen remain and defects are increased is formed. Therefore, in the source gas, a flow rate ratio of the nitrogen to the ammonia is set to be greater than or equal to 5 and less than or equal to 50, preferably greater than or equal to 10 and less than or equal to 50.

Here, a 50-nm-thick silicon nitride film is formed as the nitride insulating layer **116** using source gases of silane, nitrogen, and ammonia with a plasma CVD apparatus. The flow rates of silane, nitrogen, and ammonia are 50 sccm, 5000 sccm, and 100 sccm, respectively. The pressure in a treatment chamber is set to 100 Pa, the substrate temperature is set to 350° C., and a high frequency power of 1000 W is supplied to parallel plate electrodes using a high frequency power source of 27.12 MHz. Note that a PECVD apparatus is a parallel-plate plasma CVD apparatus in which the electrode area is 6000 cm², and the power per unit area (power density) into which the supplied power is converted is 1.7×10^{-1} W/cm².

After formation of the nitride insulating layer **116**, heat treatment may be performed. The heat treatment is performed typically at a temperature higher than or equal to 150° C. and lower than or equal to 400° C., preferably higher than or equal

25

to 300° C. and lower than or equal to 400° C., further preferably higher than or equal to 320° C. and lower than or equal to 370° C. When the heat treatment is performed, the amount of hydrogen and water of the oxide insulating layers **112** and **114** is reduced; therefore, generation of defects in the oxide semiconductor layer **106** described above is inhibited.

Next, a resist mask is formed over the nitride insulating layer **116** through a photolithography process using a photoresist mask. The nitride insulating layer **116**, the oxide insulating layers **112** and **114**, and the gate insulating layer **104** are etched using the resist mask to form the opening portions **117a** and **117b** (see FIG. **6B**).

After the resist mask is removed, a conductive film is formed over the nitride insulating layer **116** and processed to form the electrode layer **118** functioning as a back gate electrode (see FIG. **6C**).

Through the above-described process, the transistor **210** of this embodiment can be formed. Note that the other transistors of this embodiment can be formed in a manner similar to that of the transistor **210**.

As described above, since electrode layers containing a low-resistance material such as copper, aluminum, gold, or silver are used as the pair of electrode layers functioning as the source and drain electrode layers in the transistor described in this embodiment, a semiconductor device in which wiring delay is suppressed can be manufactured. Furthermore, when a metal oxide layer functioning as a barrier layer is provided in contact with the pair of electrode layers, a reduction in the electrical characteristics can be inhibited, so that the semiconductor device can have favorable electrical characteristics.

According to the manufacturing process of this embodiment, it is possible to manufacture a highly reliable transistor in which the oxygen vacancy in the oxide semiconductor layer including the channel formation region is reduced and the impurity concentration is reduced.

Furthermore, since the transistor of this embodiment is a channel-etched transistor that is formed in such a manner that the metal oxide layer **108** functioning as a barrier layer for preventing entry of impurities is formed using the same mask as the oxide semiconductor layer **106**, the number of masks can be reduced as compared to the case of a channel protective transistor. Therefore, the manufacturing cost of the semiconductor device can be reduced.

The structure and method described in this embodiment can be implemented by being combined as appropriate with any of the other structures and methods described in the other embodiments. (Embodiment 2)

The structure of an oxide semiconductor layer included in a transistor of one embodiment of the present invention is described in this embodiment.

A structure which can be included in an oxide semiconductor layer is described below.

An oxide semiconductor layer is classified into, for example, a non-single-crystal oxide semiconductor layer and a single crystal oxide semiconductor layer. Alternatively, an oxide semiconductor layer is classified into, for example, a crystalline oxide semiconductor layer and an amorphous oxide semiconductor layer.

Examples of a non-single-crystal oxide semiconductor include a c-axis aligned crystalline oxide semiconductor (CAAC-OS), a polycrystalline oxide semiconductor, a microcrystalline oxide semiconductor, and an amorphous oxide semiconductor. In addition, examples of a crystalline oxide semiconductor include a single crystal oxide semiconductor,

26

a CAAC-OS, a polycrystalline oxide semiconductor, and a microcrystalline oxide semiconductor.

First, a CAAC-OS layer is described.

A CAAC-OS layer is one of oxide semiconductor layers having a plurality of c-axis aligned crystal parts (also referred to as pellets).

In a combined analysis image (also referred to as a high-resolution TEM image) of a bright-field image and a diffraction pattern of a CAAC-OS, which is obtained using a transmission electron microscope (TEM), a plurality of pellets can be observed. However, in the high-resolution TEM image, a boundary between pellets, that is, a grain boundary is not clearly observed. Thus, in the CAAC-OS, a reduction in electron mobility due to the grain boundary is less likely to occur.

FIG. **8A** shows an example of a high-resolution TEM image of a cross section of the CAAC-OS which is obtained from a direction substantially parallel to the sample surface. Here, the TEM image is obtained with a spherical aberration corrector function. The high-resolution TEM image obtained with a spherical aberration corrector function is particularly referred to as a Cs-corrected high-resolution TEM image in the following description. Note that the Cs-corrected high-resolution TEM image can be obtained with, for example, an atomic resolution analytical electron microscope JEM-ARM200F manufactured by JEOL Ltd.

FIG. **8B** is an enlarged Cs-corrected high-resolution TEM image of a region (1) in FIG. **8A**. FIG. **8B** shows that metal atoms are arranged in a layered manner in a pellet. Each metal atom layer has a configuration reflecting unevenness of a surface over which the CAAC-OS is formed (hereinafter, the surface is referred to as a formation surface) or a top surface of the CAAC-OS, and is arranged parallel to the formation surface or the top surface of the CAAC-OS.

As shown in FIG. **8B**, the CAAC-OS has a characteristic atomic arrangement. The characteristic atomic arrangement is denoted by an auxiliary line in FIG. **8C**. FIGS. **8B** and **8C** prove that the size of a pellet is approximately 1 nm to 3 nm, and the size of a space caused by tilt of the pellets is approximately 0.8 nm. Therefore, the pellet can also be referred to as a nanocrystal (nc).

Here, according to the Cs-corrected high-resolution TEM images, the schematic arrangement of pellets **5100** of a CAAC-OS over a substrate **5120** is illustrated by such a structure in which bricks or blocks are stacked (see FIG. **8D**). The part in which the pellets are tilted as observed in FIG. **8C** corresponds to a region **5161** shown in FIG. **8D**.

For example, as shown in FIG. **23A**, a Cs-corrected high-resolution TEM image of a plane of the CAAC-OS obtained from a direction substantially perpendicular to the sample surface is observed. FIGS. **23B**, **23C**, and **23D** are enlarged Cs-corrected high-resolution TEM images of regions (1), (2), and (3) in FIG. **23A**, respectively. FIGS. **23B**, **23C**, and **23D** indicate that metal atoms are arranged in a triangular, quadrangular, or hexagonal configuration in a pellet. However, there is no regularity of arrangement of metal atoms between different pellets.

For example, when the structure of a CAAC-OS including an InGaZnO₄ crystal is analyzed by an out-of-plane method using an X-ray diffraction (XRD) apparatus, a peak appears at a diffraction angle (2θ) of around 31° as shown in FIG. **24A**. This peak is derived from the (009) plane of the InGaZnO₄ crystal, which indicates that crystals in the CAAC-OS have c-axis alignment, and that the c-axes are aligned in a direction substantially perpendicular to the formation surface or the top surface of the CAAC-OS.

Note that in structural analysis of the CAAC-OS including an InGaZnO₄ crystal by an out-of-plane method, another

peak may appear when 2θ around 36° , in addition to the peak at 2θ of around 31° . The peak at 2θ of around 36° indicates that a crystal having no c-axis alignment is included in part of the CAAC-OS. It is preferable that in the CAAC-OS, a peak appear when 2θ is around 31° and that a peak not appear when 2θ is around 36° .

On the other hand, in structural analysis of the CAAC-OS by an in-plane method in which an X-ray is incident on a sample in a direction substantially perpendicular to the c-axis, a peak appears when 2θ is around 56° . This peak is attributed to the (110) plane of the InGaZnO_4 crystal. In the case of the CAAC-OS, when analysis (ϕ scan) is performed with 2θ fixed at around 56° and with the sample rotated using a normal vector of the sample surface as an axis (ϕ axis), as shown in FIG. 24B, a peak is not clearly observed. In contrast, in the case of a single crystal oxide semiconductor of InGaZnO_4 , when ϕ scan is performed with 2θ fixed at around 56° , as shown in FIG. 24C, six peaks which are derived from crystal planes equivalent to the (110) plane are observed. Accordingly, the structural analysis using XRD shows that the directions of a-axes and b-axes are different in the CAAC-OS.

Next, FIG. 25A shows a diffraction pattern (also referred to as a selected-area transmission electron diffraction pattern) obtained in such a manner that an electron beam with a probe diameter of 300 nm is incident on an In—Ga—Zn oxide that is a CAAC-OS in a direction parallel to the sample surface. As shown in FIG. 25A, for example, spots derived from the (009) plane of an InGaZnO_4 crystal are observed. Thus, the electron diffraction also indicates that pellets included in the CAAC-OS have c-axis alignment and that the c-axes are aligned in a direction substantially perpendicular to the formation surface or the top surface of the CAAC-OS. Meanwhile, FIG. 25B shows a diffraction pattern obtained in such a manner that an electron beam with a probe diameter of 300 nm is incident on the same sample in a direction perpendicular to the sample surface. As shown in FIG. 25B, a ring-like diffraction pattern is observed. Thus, the electron diffraction also indicates that the a-axes and b-axes of the pellets included in the CAAC-OS do not have regular alignment. The first ring in FIG. 25B is considered to be derived from the (010) plane, the (100) plane, and the like of the InGaZnO_4 crystal. The second ring in FIG. 25B is considered to be derived from the (110) plane and the like.

Since the c-axes of the pellets (nanocrystals) are aligned in a direction substantially perpendicular to the formation surface or the top surface in the above manner, the CAAC-OS can also be referred to as an oxide semiconductor including c-axis aligned nanocrystals (CANC).

The CAAC-OS is an oxide semiconductor with a low impurity concentration. The impurity means an element other than the main components of the oxide semiconductor, such as hydrogen, carbon, silicon, or a transition metal element. An element (specifically, silicon or the like) having higher strength of bonding to oxygen than a metal element included in an oxide semiconductor extracts oxygen from the oxide semiconductor, which results in disorder of the atomic arrangement and reduced crystallinity of the oxide semiconductor. A heavy metal such as iron or nickel, argon, carbon dioxide, or the like has a large atomic radius (or molecular radius), and thus disturbs the atomic arrangement of the oxide semiconductor and decreases crystallinity. Additionally, the impurity contained in the oxide semiconductor might serve as a carrier trap or a carrier generation source.

Moreover, the CAAC-OS is an oxide semiconductor having a low density of defect states. For example, oxygen vacan-

cies in the oxide semiconductor serve as carrier traps or serve as carrier generation sources when hydrogen is captured therein.

In a transistor using the CAAC-OS, change in electrical characteristics due to irradiation with visible light or ultraviolet light is small.

Next, a microcrystalline oxide semiconductor layer is described.

A microcrystalline oxide semiconductor has a region in which a crystal part is observed and a region in which a crystal part is not clearly observed in a high-resolution TEM image. In most cases, the size of a crystal part included in the microcrystalline oxide semiconductor is greater than or equal to 1 nm and less than or equal to 100 nm, or greater than or equal to 1 nm and less than or equal to 10 nm. An oxide semiconductor including a nanocrystal that is a microcrystal with a size greater than or equal to 1 nm and less than or equal to 10 nm, or a size greater than or equal to 1 nm and less than or equal to 3 nm is specifically referred to as a nanocrystalline oxide semiconductor (nc-OS). In a high-resolution TEM image of the nc-OS, for example, a grain boundary is not clearly observed in some cases. Note that there is a possibility that the origin of the nanocrystal is the same as that of a pellet in a CAAC-OS. Therefore, a crystal part of the nc-OS may be referred to as a pellet in the following description.

In the nc-OS, a microscopic region (for example, a region with a size greater than or equal to 1 nm and less than or equal to 10 nm, in particular, a region with a size greater than or equal to 1 nm and less than or equal to 3 nm) has a periodic atomic arrangement. There is no regularity of crystal orientation between different pellets in the nc-OS. Thus, the orientation of the whole film is not ordered. Accordingly, the nc-OS cannot be distinguished from an amorphous oxide semiconductor, depending on an analysis method. For example, when the nc-OS is subjected to structural analysis by an out-of-plane method with an XRD apparatus using an X-ray having a diameter larger than the size of a pellet, a peak which shows a crystal plane does not appear. Furthermore, a diffraction pattern like a halo pattern is observed when the nc-OS is subjected to electron diffraction using an electron beam with a probe diameter (e.g., 50 nm or larger) that is larger than the size of a pellet (the electron diffraction is also referred to as selected-area electron diffraction). Meanwhile, spots appear in a nanobeam electron diffraction pattern of the nc-OS when an electron beam having a probe diameter close to or smaller than the size of a pellet is applied. Moreover, in a nanobeam electron diffraction pattern of the nc-OS, regions with high luminance in a circular (ring) pattern are shown in some cases. Also in a nanobeam electron diffraction pattern of the nc-OS, a plurality of spots is shown in a ring-like region in some cases.

Since there is no regularity of crystal orientation between the pellets (nanocrystals) as mentioned above, the nc-OS can also be referred to as an oxide semiconductor including non-aligned nanocrystals (NANC).

The nc-OS is an oxide semiconductor that has high regularity as compared with an amorphous oxide semiconductor. Therefore, the nc-OS is likely to have a lower density of defect states than an amorphous oxide semiconductor. Note that there is no regularity of crystal orientation between different pellets in the nc-OS. Therefore, the nc-OS has a higher density of defect states than the CAAC-OS.

Next, an amorphous oxide semiconductor is described.

The amorphous oxide semiconductor is an oxide semiconductor having disordered atomic arrangement and no crystal part and exemplified by an oxide semiconductor which exists in an amorphous state as quartz.

In a high-resolution TEM image of the amorphous oxide semiconductor, crystal parts cannot be found.

When the amorphous oxide semiconductor is subjected to structural analysis by an out-of-plane method with an XRD apparatus, a peak which shows a crystal plane does not appear. A halo pattern is observed when the amorphous oxide semiconductor is subjected to electron diffraction. Furthermore, a spot is not observed and a halo pattern appears when the amorphous oxide semiconductor is subjected to nano-beam electron diffraction.

There are various understandings of an amorphous structure. For example, a structure whose atomic arrangement does not have ordering at all is called a completely amorphous structure. Meanwhile, a structure which has ordering until the nearest neighbor atomic distance or the second-nearest neighbor atomic distance but does not have long-range ordering is also called an amorphous structure. Therefore, the strictest definition does not permit an oxide semiconductor to be called an amorphous oxide semiconductor as long as even a negligible degree of ordering is present in an atomic arrangement. At least an oxide semiconductor having long-term ordering cannot be called an amorphous oxide semiconductor. Accordingly, because of the presence of crystal part, for example, a CAAC-OS and an nc-OS cannot be called an amorphous oxide semiconductor or a completely amorphous oxide semiconductor.

Note that an oxide semiconductor may have a structure having physical properties intermediate between the nc-OS and the amorphous oxide semiconductor. The oxide semiconductor having such a structure is specifically referred to as an amorphous-like oxide semiconductor (a-like OS).

In a high-resolution TEM image of the a-like OS, a void may be observed. Furthermore, in the high-resolution TEM image, there are a region where a crystal part is clearly observed and a region where a crystal part is not observed.

A difference in effect of electron irradiation between structures of an oxide semiconductor is described below.

An a-like OS (Sample A), an nc-OS (Sample B), and a CAAC-OS (Sample C) are prepared. Each of the samples is an In—Ga—Zn oxide.

First, a high-resolution cross-sectional TEM image of each sample is obtained. The high-resolution cross-sectional TEM images show that all the samples have crystal parts.

Then, the size of the crystal part of each sample is measured. FIG. 26 shows the change in the average size of crystal parts (at 22 points to 45 points) in each sample. FIG. 26 indicates that the crystal part size in the a-like OS increases with an increase in the cumulative electron dose. Specifically, as shown by sample A, a crystal part of approximately 1.2 nm at the start of TEM observation (the crystal part is also referred to as an initial nucleus) grows to a size of approximately 2.6 nm at a cumulative electron dose of $4.2 \times 10^8 \text{ e}^-/\text{nm}^2$. In contrast, the crystal part size in the nc-OS and the CAAC-OS shows little change from the start of electron irradiation to a cumulative electron dose of $4.2 \times 10^8 \text{ e}^-/\text{nm}^2$ regardless of the cumulative electron dose. Specifically, as shown by sample B, the average crystal size is approximately 1.4 nm regardless of the observation time by TEM. Furthermore, as shown by sample C, the average crystal size is approximately 2.1 nm regardless of the observation time by TEM.

In this manner, growth of the crystal part occurs due to the crystallization of the a-like OS, which is induced by a slight amount of electron beam employed in the TEM observation. In contrast, in the nc-OS and the CAAC-OS that have good

Note that the crystal part size in the a-like OS and the nc-OS can be measured using high-resolution TEM images. For example, an InGaZnO₄ crystal has a layered structure in which two Ga—Zn—O layers are included between In—O layers. A unit cell of the InGaZnO₄ crystal has a structure in which nine layers including three In—O layers and six Ga—Zn—O layers are stacked in the c-axis direction. Accordingly, the distance between the adjacent layers is equivalent to the lattice spacing on the (009) plane (also referred to as d value). The value is calculated to be 0.29 nm from crystal structural analysis. Thus, focusing on lattice fringes in the high-resolution TEM image, each of lattice fringes in which the lattice spacing therebetween is greater than or equal to 0.28 nm and less than or equal to 0.30 nm corresponds to the a-b plane of the InGaZnO₄ crystal.

Furthermore, the density of an oxide semiconductor varies depending on the structure in some cases. For example, when the composition of an oxide semiconductor is determined, the structure of the oxide semiconductor can be expected by comparing the density of the oxide semiconductor with the density of a single crystal oxide semiconductor having the same composition as the oxide semiconductor. For example, the density of the a-like OS is higher than or equal to 78.6% and lower than 92.3% of the density of the single crystal oxide semiconductor having the same composition. For example, the density of each of the nc-OS and the CAAC-OS is higher than or equal to 92.3% and lower than 100% of the density of the single crystal oxide semiconductor having the same composition. Note that it is difficult to deposit an oxide semiconductor having a density of lower than 78% of the density of the single crystal oxide semiconductor.

Specific examples of the above description are given. For example, in the case of an oxide semiconductor having an atomic ratio of In:Ga:Zn=1:1:1, the density of single crystal InGaZnO₄ with a rhombohedral crystal structure is 6.357 g/cm³. Accordingly, in the case of the oxide semiconductor having an atomic ratio of In:Ga:Zn=1:1:1, the density of the a-like OS is higher than or equal to 5.0 g/cm³ and lower than 5.9 g/cm³. For example, in the case of the oxide semiconductor having an atomic ratio of In:Ga:Zn=1:1:1, the density of each of the nc-OS and the CAAC-OS is higher than or equal to 5.9 g/cm³ and lower than 6.3 g/cm³.

Note that there is a possibility that an oxide semiconductor having a certain composition cannot exist in a single crystal structure. In that case, single crystal oxide semiconductors with different compositions are combined at an adequate ratio, which makes it possible to calculate density equivalent to that of a single crystal oxide semiconductor with the desired composition. The density of a single crystal oxide semiconductor having the desired composition can be calculated using a weighted average according to the combination ratio of the single crystal oxide semiconductors with different compositions. Note that it is preferable to use as few kinds of single crystal oxide semiconductors as possible to calculate the density.

Note that an oxide semiconductor may be a stacked film including two or more films of an amorphous oxide semiconductor, an a-like OS, a microcrystalline oxide semiconductor, and a CAAC-OS, for example.

An oxide semiconductor having a low impurity concentration and a low density of defect states (a small number of oxygen vacancies) can have low carrier density. Therefore, such an oxide semiconductor is referred to as a highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor. A CAAC-OS and an nc-OS have a low impurity concentration and a low density of defect states as compared to an a-like OS and an amorphous oxide semiconductor. That

31

is, a CAAC-OS and an nc-OS are likely to be highly purified intrinsic or highly purified substantially intrinsic oxide semiconductors. Thus, a transistor including a CAAC-OS or an nc-OS rarely has negative threshold voltage (is rarely normally on). The highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor has few carrier traps. Therefore, a transistor including a CAAC-OS or an nc-OS has small variation in electrical characteristics and high reliability. An electric charge trapped by the carrier traps in the oxide semiconductor takes a long time to be released. The trapped electric charge may behave like a fixed electric charge. Thus, the transistor which includes the oxide semiconductor having a high impurity concentration and a high density of defect states might have unstable electrical characteristics.

<Deposition Model>

Examples of deposition models of a CAAC-OS and an nc-OS are described below.

FIG. 27A is a schematic view of the inside of a deposition chamber where a CAAC-OS is deposited by a sputtering method.

A target **5130** is attached to a backing plate. A plurality of magnets is provided to face the target **5130** with the backing plate positioned therebetween. The plurality of magnets generates a magnetic field. A sputtering method in which the disposition rate is increased by utilizing a magnetic field of magnets is referred to as a magnetron sputtering method.

The target **5130** has a polycrystalline structure in which a cleavage plane exists in at least one crystal grain.

A cleavage plane of the target **5130** including an In—Ga—Zn oxide is described as an example. FIG. 28A shows a structure of an InGaZnO₄ crystal included in the target **5130**. Note that FIG. 28A shows a structure of the case where the InGaZnO₄ crystal is observed from a direction parallel to the b-axis when the c-axis is in an upward direction.

FIG. 28A indicates that oxygen atoms in a Ga—Zn—O layer are positioned close to those in an adjacent Ga—Zn—O layer. The oxygen atoms have negative charge, whereby the two Ga—Zn—O layers repel each other. As a result, the InGaZnO₄ crystal has a cleavage plane between the two adjacent Ga—Zn—O layers.

The substrate **5120** is placed to face the target **5130**, and the distance d (also referred to as a target-substrate distance (T-S distance)) is greater than or equal to 0.01 m and less than or equal to 1 m, preferably greater than or equal to 0.02 m and less than or equal to 0.5 m. The deposition chamber is mostly filled with a deposition gas (e.g., an oxygen gas, an argon gas, or a mixed gas containing oxygen at 5 vol % or higher) and the pressure in the deposition chamber is controlled to be higher than or equal to 0.01 Pa and lower than or equal to 100 Pa, preferably higher than or equal to 0.1 Pa and lower than or equal to 10 Pa. Here, discharge starts by application of a voltage at a certain value or higher to the target **5130**, and plasma is observed. The magnetic field forms a high-density plasma region in the vicinity of the target **5130**. In the high-density plasma region, the deposition gas is ionized, so that an ion **5101** is generated. Examples of the ion **5101** include an oxygen cation (O⁺) and an argon cation (Ar⁺).

The ion **5101** is accelerated toward the target **5130** side by an electric field, and then collides with the target **5130**. At this time, a pellet **5100a** and a pellet **5100b** which are flat-plate-like (pellet-like) sputtered particles are separated and sputtered from the cleavage plane. Note that structures of the pellet **5100a** and the pellet **5100b** may be distorted by an impact of collision of the ion **5101**.

The pellet **5100a** is a flat-plate-like (pellet-like) sputtered particle having a triangle plane, e.g., regular triangle plane.

32

The pellet **5100b** is a flat-plate-like (pellet-like) sputtered particle having a hexagon plane, e.g., regular hexagon plane. Note that flat-plate-like (pellet-like) sputtered particles such as the pellet **5100a** and the pellet **5100b** are collectively called pellets **5100**. The shape of a flat plane of the pellet **5100** is not limited to a triangle or a hexagon. For example, the flat plane may have a shape formed by combining two or more triangles. For example, a quadrangle (e.g., rhombus) may be formed by combining two triangles (e.g., regular triangles).

The thickness of the pellet **5100** is determined depending on the kind of deposition gas and the like. The thicknesses of the pellets **5100** are preferably uniform; the reason for this is described later. In addition, the sputtered particle preferably has a pellet shape with a small thickness as compared to a dice shape with a large thickness. For example, the thickness of the pellet **5100** is greater than or equal to 0.4 nm and less than or equal to 1 nm, preferably greater than or equal to 0.6 nm and less than or equal to 0.8 nm. In addition, for example, the width of the pellet **5100** is greater than or equal to 1 nm and less than or equal to 3 nm, preferably greater than or equal to 1.2 nm and less than or equal to 2.5 nm. The pellet **5100** corresponds to the initial nucleus in the description of (1) in FIG. 26. For example, in the case where the ion **5101** collides with the target **5130** including an In—Ga—Zn oxide, the pellet **5100** that includes three layers of a Ga—Zn—O layer, an In—O layer, and a Ga—Zn—O layer as shown in FIG. 28B is ejected. Note that FIG. 28C shows the structure of the pellet **5100** observed from a direction parallel to the c-axis. Therefore, the pellet **5100** has a nanometer-sized sandwich structure including two Ga—Zn—O layers (pieces of bread) and an In—O layer (filling).

The pellet **5100** may receive a charge when passing through the plasma, so that side surfaces thereof are negatively or positively charged. The pellet **5100** includes an oxygen atom on its side surface, and the oxygen atom may be negatively charged. In this manner, when the side surfaces are charged with the same polarity, charges repel each other, and accordingly, the pellet **5100** can maintain a flat-plate shape. In the case where a CAAC-OS is an In—Ga—Zn oxide, there is a possibility that an oxygen atom bonded to an indium atom is negatively charged. There is another possibility that an oxygen atom bonded to an indium atom, a gallium atom, or a zinc atom is negatively charged. In addition, the pellet **5100** may grow by being bonded with an indium atom, a gallium atom, a zinc atom, an oxygen atom, or the like when passing through plasma. A difference in size between (2) and (1) in FIG. 26 corresponds to the amount of growth in plasma. Here, in the case where the temperature of the substrate **5120** is at around room temperature, the pellet **5100** does not grow anymore, thus, an nc-OS is formed (see FIG. 27B). An nc-OS can be deposited when the substrate **5120** has a large size because a temperature at which the deposition of an nc-OS is carried out is approximately room temperature. Note that in order that the pellet **5100** grows in plasma, it is effective to increase deposition power in sputtering. High deposition power can stabilize the structure of the pellet **5100**.

As shown in FIGS. 27A and 27B, the pellet **5100** flies like a kite in plasma and flutters up to the substrate **5120**. Since the pellets **5100** are charged, when the pellet **5100** gets close to a region where another pellet **5100** has already been deposited, repulsion is generated. Here, above the substrate **5120**, a magnetic field in a direction parallel to the top surface of the substrate **5120** (also referred to as a horizontal magnetic field) is generated. A potential difference is given between the substrate **5120** and the target **5130**, and accordingly, current flows from the substrate **5120** toward the target **5130**. Thus, the pellet **5100** is given a force (Lorentz force) on the top

surface of the substrate **5120** by an effect of the magnetic field and the current. This is explainable with Fleming's left-hand rule.

The mass of the pellet **5100** is larger than that of an atom. Therefore, to move the pellet **5100** over the top surface of the substrate **5120**, it is important to apply some force to the pellet **5100** from the outside. One kind of the force may be force which is generated by the action of a magnetic field and current. In order to increase a force applied to the pellet **5100**, it is preferable to provide, on the top surface, a region where the magnetic field in a direction parallel to the top surface of the substrate **5120** is 10 G or higher, preferably 20 G or higher, further preferably 30 G or higher, still further preferably 50 G or higher. Alternatively, it is preferable to provide, on the top surface, a region where the magnetic field in a direction parallel to the top surface of the substrate **5120** is 1.5 times or higher, preferably twice or higher, further preferably 3 times or higher, still further preferably 5 times or higher as high as the magnetic field in a direction perpendicular to the top surface of the substrate **5120**.

At this time, the magnets and the substrate **5120** are moved or rotated relatively, whereby the direction of the horizontal magnetic field on the top surface of the substrate **5120** continues to change. Therefore, the pellet **5100** can be moved in various directions on the top surface of the substrate **5120** by receiving forces in various directions.

Furthermore, as shown in FIG. 27A, when the substrate **5120** is heated, resistance between the pellet **5100** and the substrate **5120** due to friction or the like is low. As a result, the pellet **5100** glides above the top surface of the substrate **5120**. The glide of the pellet **5100** is caused in a state where its flat plane faces the substrate **5120**. Then, when the pellet **5100** reaches the side surface of another pellet **5100** that has been already deposited, the side surfaces of the pellets **5100** are bonded. At this time, the oxygen atom on the side surface of the pellet **5100** is released. With the released oxygen atom, oxygen vacancies in a CAAC-OS might be filled; thus, the CAAC-OS has a low density of defect states. Note that the temperature of the top surface of the substrate **5120** is, for example, higher than or equal to 100° C. and lower than 500° C., higher than or equal to 150° C. and lower than 450° C., or higher than or equal to 170° C. and lower than 400° C. Hence, even when the substrate **5120** has a large size, it is possible to deposit a CAAC-OS.

Furthermore, the pellet **5100** is heated on the substrate **5120**, whereby atoms are rearranged, and the structure distortion caused by the collision of the ion **5101** can be reduced. The pellet **5100** whose structure distortion is reduced is substantially single crystal. Even when the pellets **5100** are heated after being bonded, expansion and contraction of the pellet **5100** itself hardly occur, which is caused by turning the pellet **5100** into substantially single crystal. Thus, formation of defects such as a grain boundary due to expansion of a space between the pellets **5100** can be prevented, and accordingly, generation of crevasses can be prevented.

The CAAC-OS does not have a structure like a board of a single crystal oxide semiconductor but has arrangement with a group of pellets **5100** (nanocrystals) like stacked bricks or blocks. Furthermore, a grain boundary does not exist therebetween. Therefore, even when deformation such as shrink occurs in the CAAC-OS owing to heating during deposition, heating or bending after deposition, it is possible to relieve local stress or release distortion. Therefore, this structure is suitable for a flexible semiconductor device. Note that the nc-OS has arrangement in which pellets **5100** (nanocrystals) are randomly stacked.

When the target is sputtered with an ion, in addition to the pellets, zinc oxide or the like may be ejected. The zinc oxide is lighter than the pellet and thus reaches the top surface of the substrate **5120** before the pellet. As a result, the zinc oxide forms a zinc oxide layer **5102** with a thickness greater than or equal to 0.1 nm and less than or equal to 10 nm, greater than or equal to 0.2 nm and less than or equal to 5 nm, or greater than or equal to 0.5 nm and less than or equal to 2 nm. FIGS. 29A to 29D are cross-sectional schematic views.

As illustrated in FIG. 29A, a pellet **5105a** and a pellet **5105b** are deposited over the zinc oxide layer **5102**. Here, side surfaces of the pellet **5105a** and the pellet **5105b** are in contact with each other. In addition, a pellet **5105c** is deposited over the pellet **5105b**, and then glides over the pellet **5105b**. Furthermore, a plurality of particles **5103** ejected from the target together with the zinc oxide is crystallized by heating of the substrate **5120** to form a region **5105a1** on another side surface of the pellet **5105a**. Note that the plurality of particles **5103** may contain oxygen, zinc, indium, gallium, or the like.

Then, as illustrated in FIG. 29B, the region **5105a1** grows to part of the pellet **5105a** to form a pellet **5105a2**. In addition, a side surface of the pellet **5105c** is in contact with another side surface of the pellet **5105b**.

Next, as illustrated in FIG. 29C, a pellet **5105d** is deposited over the pellet **5105a2** and the pellet **5105b**, and then glides over the pellet **5105a2** and the pellet **5105b**. Furthermore, a pellet **5105e** glides toward another side surface of the pellet **5105c** over the zinc oxide layer **5102**.

Then, as illustrated in FIG. 29D, the pellet **5105d** is placed so that a side surface of the pellet **5105d** is in contact with a side surface of the pellet **5105a2**. Furthermore, a side surface of the pellet **5105e** is in contact with another side surface of the pellet **5105c**. A plurality of particles **5103** ejected from the target together with the zinc oxide is crystallized by heating of the substrate **5120** to form a region **5105d** on another side surface of the pellet **5105d**.

As described above, deposited pellets are placed to be in contact with each other and then growth is caused at side surfaces of the pellets, whereby a CAAC-OS is formed over the substrate **5120**. Therefore, each pellet of the CAAC-OS is larger than that of the nc-OS. A difference in size between (3) and (2) in FIG. 26 corresponds to the amount of growth after deposition.

When spaces between pellets **5100** are extremely small, the pellets may form a large pellet. The large pellet has a single crystal structure. For example, the size of the large pellet may be greater than or equal to 10 nm and less than or equal to 200 nm, greater than or equal to 15 nm and less than or equal to 100 nm, or greater than or equal to 20 nm and less than or equal to 50 nm, when seen from the above. Therefore, when a channel formation region of a transistor is smaller than the large pellet, the region having a single crystal structure can be used as the channel formation region. Furthermore, when the size of the pellet is increased, the region having a single crystal structure can be used as the channel formation region, the source region, and the drain region of the transistor.

In this manner, when the channel formation region or the like of the transistor is formed in a region having a single crystal structure, the frequency characteristics of the transistor can be increased in some cases.

As shown in such a model, the pellets **5100** are considered to be deposited on the substrate **5120**. Thus, a CAAC-OS can be deposited even when a formation surface does not have a crystal structure, which is different from film deposition by epitaxial growth. For example, even when the top surface (formation surface) of the substrate **5120** has an amorphous

structure (e.g. the top surface is formed of amorphous silicon oxide), a CAAC-OS can be formed.

In addition, it is found that in formation of the CAAC-OS, the pellets **5100** are arranged in accordance with the top surface shape of the substrate **5120** that is the formation surface even when the formation surface has unevenness. For example, in the case where the top surface of the substrate **5120** is flat at the atomic level, the pellets **5100** are arranged so that flat planes parallel to the a-b plane face downwards. In the case where the thicknesses of the pellets **5100** are uniform, a layer with a uniform thickness, flatness, and high crystallinity is formed. By stacking n layers (n is a natural number), the CAAC-OS can be obtained.

In the case where the top surface of the substrate **5120** has unevenness, a CAAC-OS in which n layers (n is a natural number) in each of which the pellets **5100** are arranged along the unevenness are stacked is formed. Since the substrate **5120** has unevenness, a gap is easily generated between the pellets **5100** in the CAAC-OS in some cases. Note that owing to intermolecular force, the pellets **5100** are arranged so that a gap between the pellets is as small as possible even on the unevenness surface. Therefore, even when the formation surface has unevenness, a CAAC-OS with high crystallinity can be obtained.

As a result, laser crystallization is not needed for formation of a CAAC-OS, and a uniform film can be formed even over a large-sized glass substrate or the like.

Since a CAAC-OS is deposited in accordance with such a model, the sputtered particle preferably has a pellet shape with a small thickness. Note that when the sputtered particles have a dice shape with a large thickness, planes facing the substrate **5120** vary; thus, the thicknesses and orientations of the crystals cannot be uniform in some cases.

According to the deposition model described above, a CAAC-OS with high crystallinity can be formed even on a formation surface with an amorphous structure.

FIG. 9C illustrates a transmission electron diffraction measurement apparatus which includes an electron gun chamber **10**, an optical system **12** below the electron gun chamber **10**, a sample chamber **14** below the optical system **12**, an optical system **16** below the sample chamber **14**, an observation chamber **20** below the optical system **16**, a camera **18** installed in the observation chamber **20**, and a film chamber **22** below the observation chamber **20**. The camera **18** is provided to face toward the inside of the observation chamber **20**. Note that the film chamber **22** is not necessarily provided.

FIG. 9D illustrates an internal structure of the transmission electron diffraction measurement apparatus illustrated in FIG. 9C. In the transmission electron diffraction measurement apparatus, a substance **28** which is positioned in the sample chamber **14** is irradiated with electrons emitted from an electron gun installed in the electron gun chamber **10** through the optical system **12**. Electrons passing through the substance **28** enter a fluorescent plate **32** provided in the observation chamber **20** through the optical system **16**. On the fluorescent plate **32**, a pattern corresponding to the intensity of entered electron appears, which allows measurement of a transmission electron diffraction pattern.

The camera **18** is installed so as to face the fluorescent plate **32** and can take a picture of a pattern appearing in the fluorescent plate **32**. An angle which is formed by a line passing through the center of a lens of the camera **18** and the top surface of the fluorescent plate **32**, and a line which passes through the center of the lens of the camera **18** and is perpendicular to a floor is, for example, greater than or equal to 15° and less than or equal to 80°, greater than or equal to 30° and less than or equal to 75°, or greater than or equal to 45° and

less than or equal to 70°. As the angle is reduced, distortion of the transmission electron diffraction pattern taken by the camera **18** becomes larger. Note that if the angle is obtained in advance, the distortion of an obtained transmission electron diffraction pattern can be corrected. Note that the film chamber **22** may be provided with the camera **18**. For example, the camera **18** may be set in the film chamber **22** so as to be opposite to the incident direction of electrons **24** enter. In this case, a transmission electron diffraction pattern with less distortion can be taken from the rear surface of the fluorescent plate **32**.

A holder for fixing the substance **28** that is a sample is provided in the sample chamber **14**. The holder transmits electrons passing through the substance **28**. The holder may have, for example, a function of moving the substance **28** in the direction of the X, Y, and Z axes. The movement function of the holder may have an accuracy of moving the substance in the range of, for example, 1 nm to 10 nm, 5 nm to 50 nm, 10 nm to 100 nm, 50 nm to 500 nm, and 100 nm to 1 μ m. The range is preferably determined to be an optimal range for the structure of the substance **28**.

Then, a method for measuring a transmission electron diffraction pattern of a substance by the transmission electron diffraction measurement apparatus described above is described.

For example, changes in the structure of a substance can be observed by changing (scanning) the irradiation position of the electrons **24** that are a nanobeam in the substance, as illustrated in FIG. 9D. At this time, when the substance **28** is a CAAC-OS film, a diffraction pattern shown in FIG. 9A can be observed. When the substance **28** is an nc-OS film, a diffraction pattern shown in FIG. 9B can be observed.

Even when the substance **28** is a CAAC-OS film, a diffraction pattern similar to that of an nc-OS film or the like is partly observed in some cases. Therefore, whether or not the CAAC-OS film is favorable can be determined by the proportion of a region where a diffraction pattern of the CAAC-OS film is observed in a predetermined area (also referred to as proportion of CAAC). For example, in the case of a favorable CAAC-OS film, the proportion of CAAC is 60% or higher, preferably 80% or higher, further preferably 90% or higher, still preferably 95% or higher. Note that a region where a diffraction pattern different from that of a CAAC-OS film is observed is referred to as the proportion of non-CAAC.

For example, transmission electron diffraction patterns were obtained by scanning a top surface of a sample including a CAAC-OS film obtained just after deposition (represented as "as-sputtered") and a top surface of a sample including a CAAC-OS subjected to heat treatment at 450° C. in an atmosphere containing oxygen. Here, the proportion of CAAC was obtained in such a manner that diffraction patterns were observed by scanning for 60 seconds at a rate of 5 nm/second and the obtained diffraction patterns were converted into still images every 0.5 seconds. Note that as an electron beam, a nano-electron beam with a probe diameter of 1 nm was used. The above measurement was performed on six samples. The proportion of CAAC was calculated using the average value of the six samples.

FIG. 10A shows the proportion of CAAC in each sample. The proportion of CAAC of the CAAC-OS film obtained just after the deposition was 75.7% (the proportion of non-CAAC was 24.3%). The proportion of CAAC of the CAAC-OS film subjected to the heat treatment at 450° C. was 85.3% (the proportion of non-CAAC was 14.7%). These results show that the proportion of CAAC obtained after the heat treatment at 450° C. is higher than that obtained just after the deposition. That is, heat treatment at a high temperature (e.g., higher than

or equal to 400° C.) reduces the proportion of non-CAAC (increases the proportion of CAAC). Furthermore, the above results also indicate that even when the temperature of the heat treatment is lower than 500° C., the CAAC-OS film can have a high proportion of CAAC.

Here, most of diffraction patterns different from that of a CAAC-OS film are diffraction patterns similar to that of an nc-OS film. Furthermore, an amorphous oxide semiconductor film was not able to be observed in the measurement region. Therefore, the above results suggest that the region having a structure similar to that of an nc-OS film is rearranged by the heat treatment owing to the influence of the structure of the adjacent region, whereby the region becomes CAAC.

FIGS. 10B and 10C are planar TEM images of the CAAC-OS film obtained just after the deposition and the CAAC-OS film subjected to the heat treatment at 450° C., respectively. Comparison between FIGS. 10B and 10C shows that the CAAC-OS film subjected to the heat treatment at 450° C. has more uniform film quality. That is, the heat treatment at a high temperature improves the film quality of the CAAC-OS film.

With such a measurement method, the structure of an oxide semiconductor layer having a plurality of structures can be analyzed in some cases.

The transistor of one embodiment of the present invention can be formed using an oxide semiconductor layer having any of the above structures.

The structure and method described in this embodiment can be implemented by being combined as appropriate with any of the other structures and methods described in the other embodiments.

(Embodiment 3)

In this embodiment, a semiconductor device which includes a transistor having a different structure from that of Embodiment 1 is described with reference to FIGS. 7A to 7C. The transistor described in this embodiment is different from those in Embodiment 1 in that a multilayer film including a plurality of oxide semiconductor layers is provided. Here, details of the transistor are described using the semiconductor device illustrated in FIGS. 2A and 2B in Embodiment 1.

FIGS. 7A and 7B are a plan view and a cross-sectional view of a transistor 310 included in the semiconductor device of this embodiment. FIG. 7A is a plan view of the transistor 310, and FIG. 7B is cross-sectional views taken along dashed dotted lines A9-A10 and B9-B10 in FIG. 7A. Note that the substrate 100 and some components (e.g., a gate insulating layer) of the transistor 310 are not illustrated in FIG. 7A for clarity. FIG. 7C shows a band diagram of a stacked-layer structure included in the transistor 310.

The transistor 310 included in the semiconductor device illustrated in FIGS. 7A to 7C is different from the transistor 210 in FIGS. 2A and 2B in that the oxide semiconductor layer provided between the gate insulating layer 104 and the metal oxide layer 108 has a stacked-layer structure including an oxide semiconductor layer 306a and an oxide semiconductor layer 306b. The other components are similar to those in FIGS. 2A and 2B; thus, the above description can be referred to.

The oxide semiconductor layer 306a and the oxide semiconductor layer 306b in the transistor 310 are each formed using a metal oxide containing at least In or Zn; as a typical example, an In—Ga oxide, an In—Zn oxide, or an In—M—Zn oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) can be used. The energy of the bottom of the conduction band of the oxide semiconductor layer 306b is closer to the vacuum level than that of the oxide semiconductor layer 306a; typically, an energy difference between the bottom of the conduction band

of the oxide semiconductor layer 306b and the bottom of the conduction band of the oxide semiconductor layer 306a is greater than or equal to 0.05 eV, greater than or equal to 0.07 eV, greater than or equal to 0.1 eV, greater than or equal to 0.15 eV, or greater than or equal to 0.5 eV, and less than or equal to 2 eV or less than or equal to 1 eV. That is, the difference between the electron affinity of the oxide semiconductor layer 306b and the electron affinity of the oxide semiconductor layer 306a is greater than or equal to 0.05 eV, greater than or equal to 0.07 eV, greater than or equal to 0.1 eV, greater than or equal to 0.15 eV, or greater than or equal to 0.5 eV and also less than or equal to 2 eV, or less than or equal to 1 eV.

In such a structure, the oxide semiconductor layer 306a serves as a main path of current and functions as a channel region when voltage is applied to the transistor 310. In addition, since the oxide semiconductor layer 306b contains one or more kinds of metal elements that are contained in the oxide semiconductor layer 306a where the channel is formed, interface scattering is less likely to occur at the interface between the oxide semiconductor layer 306a and the oxide semiconductor layer 306b. Thus, the transistor can have high field-effect mobility because the movement of carriers is not hindered at the interface.

When the oxide semiconductor layer 306b is formed of an In—M—Zn oxide in which the atomic ratio of the element M (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) is higher than that of In, the energy gap of the oxide semiconductor layer 306b can be large and the electron affinity can be small. Therefore, a difference in electron affinity between the oxide semiconductor layer 306a and the oxide semiconductor layer 306b may be controlled by the proportion of the element M. Furthermore, oxygen vacancy is less likely to be generated in the oxide semiconductor layer in which the atomic ratio of Ti, Ga, Y, Zr, La, Ce, Nd, or Hf is higher than that of In because Ti, Ga, Y, Zr, La, Ce, Nd, and Hf each are a metal element that is strongly bonded to oxygen.

In the case where the oxide semiconductor layer 306b is formed of an In—M—Zn oxide, when Zn and O are eliminated from consideration, the atomic percentage of In and the atomic percentage of M are preferably less than 50 atomic % and greater than or equal to 50 atomic %, respectively, more preferably less than 25 atomic % and greater than or equal to 75 atomic %, respectively.

Furthermore, in the case where each of the oxide semiconductor layer 306a and the oxide semiconductor layer 306b is formed of In—M—Zn oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf), the atomic percent of M (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) in the oxide semiconductor layer 306b is higher than that in the oxide semiconductor layer 306a. Typically, the atomic percentage of M in the oxide semiconductor layer 306b is 1.5 or more times, twice or more, or three or more times as high as that in the oxide semiconductor layer 306a.

Furthermore, in the case where each of the oxide semiconductor layer 306a and the oxide semiconductor layer 306b is formed of an In—M—Zn oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf), when the oxide semiconductor layer 306a has an atomic ratio of In:M:Zn= $x_1:y_1:z_1$ and the oxide semiconductor layer 306b has an atomic ratio of In:M:Zn= $x_2:y_2:z_2$, y_2/x_2 is higher than y_1/x_1 . It is preferable that y_2/x_2 be 1.5 or more times as high as y_1/x_1 . It is further preferable that y_2/x_2 be twice or more as high as y_1/x_1 . It is still further preferable that y_2/x_2 be three or more times as high as y_1/x_1 . In this case, it is preferable that in the oxide semiconductor layer, y_1 be higher than or equal to x_1 because a transistor including the oxide semiconductor layer can have stable electric characteristics. However, when y_1 is higher than or equal to three times x_1 , the

field-effect mobility of the transistor including the oxide semiconductor layer is reduced. Thus, it is preferable that y_1 be lower than three times x_1 . The composition of the oxide semiconductor layer can be measured by ICP-MS. For example, a metal oxide film that is obtained under conditions where a target with $\text{In}_2\text{O}_3:\text{Ga}_2\text{O}_3:\text{ZnO}=1:1:1$ ($\text{In}:\text{Ga}:\text{Zn}=1:1:0.5$) is used and the flow ratio of an argon gas in a sputtering method is 40 sccm is $\text{InGa}_{0.95}\text{ZnO}_{0.41}\text{O}_{3.33}$. Furthermore, the composition can be quantified using a Rutherford backscattering spectrometry (RBS) instead of ICP-MS.

In the case where the oxide semiconductor layer **306a** is formed of an In-M-Zn oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) and a target having the atomic ratio of metal elements of $\text{In}:\text{M}:\text{Zn}=x_1:y_1:z_1$ is used for depositing the oxide semiconductor layer **306a**, x_1/y_1 is preferably greater than or equal to $1/3$ and less than or equal to 6, further preferably greater than or equal to 1 and less than or equal to 6, and z_1/y_1 is preferably greater than or equal to $1/3$ and less than or equal to 6, further preferably greater than or equal to 1 and less than or equal to 6. Note that when z_1/y_1 is greater than or equal to 1 and less than or equal to 6, CAAC-OS film is easily formed as the oxide semiconductor layer **306a**. Typical examples of the atomic ratio of the metal elements of the target include $\text{In}:\text{M}:\text{Zn}=1:1:1$ and $\text{In}:\text{M}:\text{Zn}=3:1:2$.

Note that in the case where a target with $\text{In}:\text{M}:\text{Zn}=1:1:z_{10}$ is used for depositing the oxide semiconductor layer **306a**, z_{10} is preferably greater than or equal to 1 and less than or equal to 1.4, further preferably greater than or equal to 1 and less than or equal to 1.3. This is because, for example, when $\text{In}:\text{M}:\text{Zn}=1:1:1.5$, the target becomes opaque, and sputtering deposition with a DC power source or an AC power source might become difficult. Such a target is applicable to deposition using an RF power source; however, in consideration of productivity of the semiconductor device, it is preferable to use a target which is applicable to a sputtering deposition using a DC power source or an AC power source.

In the case where the oxide semiconductor layer **306b** is formed of an In-M-Zn oxide (M is Ti, Ga, Y, Zr, La, Ce, Nd, or Hf) and a target having an atomic ratio of metal elements of $\text{In}:\text{M}:\text{Zn}=x_2:y_2:z_2$ is used for depositing the oxide semiconductor layer **306b**, x_2/y_2 is preferably less than x_1/y_1 , and z_2/y_2 is preferably greater than or equal to $1/3$ and less than or equal to 6, further preferably greater than or equal to 1 and less than or equal to 6. When the atomic ratio of M with respect to indium is high, the energy gap of the oxide semiconductor layer **306b** can be large and the electron affinity thereof can be small; therefore, y_2/x_2 is preferably higher than or equal to 3 or higher than or equal to 4. Typical examples of the atomic ratio of the metal elements of the target include $\text{In}:\text{M}:\text{Zn}=1:3:2$, $\text{In}:\text{M}:\text{Zn}=1:3:4$, $\text{In}:\text{M}:\text{Zn}=1:3:5$, $\text{In}:\text{M}:\text{Zn}=1:3:6$, $\text{In}:\text{M}:\text{Zn}=1:4:2$, $\text{In}:\text{M}:\text{Zn}=1:4:4$, and $\text{In}:\text{M}:\text{Zn}=1:4:5$.

For example, in the case where a target with $\text{In}:\text{M}:\text{Zn}=1:3:z_{20}$ is used as the target for depositing the oxide semiconductor layer **306b**, z_{20} is preferably greater than or equal to 2 and less than or equal to 5. Alternatively, in the case where a target having an atomic ratio of $\text{In}:\text{M}:\text{Zn}=1:4:z_{30}$ is used for depositing the oxide semiconductor layer **306b**, z_{30} is preferably greater than or equal to 2 and less than or equal to 5.

Note that in each of the oxide semiconductor layer **306a** and the oxide semiconductor layer **306b**, the proportions of atoms in the atomic ratio varies within a range of $\pm 40\%$ as an error.

It is preferable that the oxide semiconductor layer **306a** and the oxide semiconductor layer **306b** have crystal parts, further preferably, have the same crystal structures. This is because when the oxide semiconductor layer **306a** and the oxide semiconductor layer **306b** have different crystal structures, the

interface between the layers becomes a hetero crystalline structure part and a defect might be generated therein. The hetero crystalline structure part can be regarded as, for example, a grain boundary.

As the oxide semiconductor layer **306a**, a CAAC-OS film that is an oxide semiconductor layer having a low impurity concentration and low density of defect states (a small amount of oxygen vacancy) is preferably used. The state in which impurity concentration is low and density of defect states is low is referred to as highly purified intrinsic or highly purified substantially intrinsic. A highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor layer has few carrier generation sources, and thus has a low carrier density. Thus, a transistor using the oxide semiconductor layer as a channel rarely has electrical characteristics in which a threshold voltage is negative (also referred to as normally-on). A highly purified intrinsic or highly purified substantially intrinsic oxide semiconductor layer has few carrier traps. Thus, the transistor including the oxide semiconductor layer in the channel has a small variation in electrical characteristics and high reliability. With the use of the CAAC-OS film in a transistor, variation in the electrical characteristics of the transistor due to irradiation with visible light or ultraviolet light is small.

Note that it is preferable that a target with $\text{In}:\text{M}:\text{Zn}=1:1:1.2$ be used for depositing the oxide semiconductor layer **306a** because a spinel structure is less likely to be formed in the deposited oxide semiconductor layer **306a**, so that the proportion of CAAC can be increased.

Furthermore, in the case where the oxide semiconductor layer **306a** is a CAAC-OS film and the oxide semiconductor layer **306b** in contact with the oxide semiconductor layer **306a** has a different crystal structure, a grain boundary is formed at the interface between the two layers and a defect might be formed in the film; therefore, it is preferable to use a CAAC-OS film also for the oxide semiconductor layer **306b**.

Meanwhile, in the case where, for example, an In—Ga oxide layer is formed as the metal oxide layer **108**, which functions as a barrier layer for preventing mixing of impurities to the oxide semiconductor layers **306a** and **306b**, the In—Ga oxide layer can have an amorphous structure, a crystalline structure similar to that of an nc-OS film, or a monoclinic structure; however, it is difficult for the In—Ga oxide layer to have a crystalline structure similar to that of a CAAC-OS film. Therefore, when the oxide semiconductor layer **306a** where the channel is formed is in contact with the metal oxide layer **108**, a hetero structure might be formed at the interface between the two layers. In the transistor **310** described in this embodiment, since the oxide semiconductor layer **306b** is provided between the metal oxide layer **108** and the oxide semiconductor layer **306a** where the channel is formed, the region in contact with the hetero structure can be apart from the oxide semiconductor layer **306a** where carriers flow. However, the oxide semiconductor layer **306b** may have a spinel structure therein. This is because the metal oxide layer **108** can prevent the constituent elements of the pair of electrode layers **110a** and **110b** from diffusing into the oxide semiconductor layer **306b**; therefore, even when the oxide semiconductor layer **306b** has a spinel structure, diffusion of a metal element such as copper which is derived from the spinel structure, to the channel can be prevented.

FIG. 7C is an example of a band structure in the thickness direction of the stacked-layer structure including the gate insulating layer **104**, the oxide semiconductor layer **306a**, the oxide semiconductor layer **306b**, the metal oxide layer **108**, and the oxide insulating layer **112**. For easy understanding,

41

the energy (E_c) of the bottom of the conduction band of each of the gate insulating layer **104**, the oxide semiconductor layer **306a**, the oxide semiconductor layer **306b**, the metal oxide layer **108**, and the oxide insulating layer **112** is shown in the band structure.

As shown in FIG. 7C, there is no energy barrier between the oxide semiconductor layers **306a** and **306b**, and the energy of the bottom of the conduction band is changed smoothly (such a state is also referred to as a continuous junction). In other words, the energy of the bottom of the conduction band is continuously changed. To obtain such a band structure, it is preferable that an impurity which forms a defect level such as a trap center or a recombination center does not exist at the interface between the oxide semiconductor layer **306a** and the oxide semiconductor layer **306b**. This is because if an impurity exists between the stacked oxide semiconductor layers, a continuity of the energy band is damaged, and the carrier is captured or recombined at the interface and then disappears.

To form a continuous junction between the oxide semiconductor layers **306a** and **306b**, it is necessary to form films continuously without being exposed to air, with use of a multi-chamber deposition apparatus (sputtering apparatus) including a load lock chamber.

With the structure of FIG. 7C, the oxide semiconductor layer **306a** serves as a well, and a channel region is formed in the oxide semiconductor layer **306a** in the transistor with the stacked layer structure.

Although trap levels due to impurities or defects might be formed in the vicinity of the interface between the metal oxide layer **108** and the oxide insulating layer **112** as shown in FIG. 8A, the oxide semiconductor layers **306a** and **306b** can be distanced from the trap levels owing to the existence of the metal oxide layer **108**. Furthermore, even when defects due to the hetero crystalline structure exist between the metal oxide layer **108** and the oxide semiconductor layer **306b**, the oxide semiconductor layer **306b** can reduce the influence of the defects upon the oxide semiconductor layer **306a**. Here, in the case where an energy difference between the bottom of the conduction band of the oxide semiconductor layer **306a** and that of the oxide semiconductor layer **306b** is small, electrons in the oxide semiconductor layer **306a** might reach the trap level by passing through the energy difference. Since the electron is trapped at the trap level, a negative fixed charge is generated, causing the threshold voltage of the transistor to be shifted in the positive direction. Thus, it is preferable that the energy difference between the bottom of the conduction band of the oxide semiconductor layer **306a** and that of the oxide semiconductor layer **306b** be 0.1 eV or more, preferably 0.15 eV or more because a change in the threshold voltage of the transistor is reduced and stable electrical characteristics are obtained.

It is preferable that the difference in energy of the bottom of the conduction band between the oxide semiconductor layer **306a** and the oxide semiconductor layer **306b** be greater than or equal to 0.1 eV, further preferably greater than or equal to 0.15 eV because the trap level existing in the vicinity of the interface between the metal oxide layer **108** and the oxide insulating layer **112** can be prevented from affecting the oxide semiconductor layer **306b** and the oxide semiconductor layer **306a** in contact with the oxide semiconductor layer **306b**.

Note that the structure of the transistor having the stacked-layer structure that is described in this embodiment is not limited to that of FIGS. 7A to 7C. For example, like in a transistor **300** illustrated in FIG. 21A, the oxide semiconductor layer provided between the gate insulating layer **104** and the metal oxide layer **108** may have a stacked-layer structure

42

including an oxide semiconductor layer **316a** and an oxide semiconductor layer **316b** in the structure of the transistor **200** described in Embodiment 1. Note that FIG. 21A illustrates a cross section of the transistor **300** in the channel length direction and a cross section of a connection portion between an electrode layer **202b** which is formed in the same layer as a gate electrode layer **202a** and an electrode layer **110c** which is formed in the same layer as the pair of electrode layers **110a** and **110b**.

In the transistor **300** in FIG. 21A, the gate electrode layer **202a** and the electrode layer **202b** that is formed in the same layer as the gate electrode layer **202a** have a stacked-layer structure including first conductive layers **101a** and **101b** and a stacked-layer structure including second conductive layers **103a** and **103b**, respectively. A material similar to that of the first conductive layer **109a** and **109b** of the pair of electrode layers **110a** and **110b** can be used for the first conductive layers **101a** and **101b**. A material similar to that of the second conductive layers **111a** and **111b** of the pair of electrode layers **110a** and **110b** can be used for the second conductive layers **103a** and **103b**.

When the gate electrode layer **202a** and the electrode layer **202b** are formed to contain a low-resistance material such as copper, aluminum, gold, or silver, it is possible to manufacture a semiconductor device with reduced wiring delay even in the case of using a large-sized substrate as the substrate **100**. Note that in the case where electrode layers containing any of the above low-resistance materials are formed as the gate electrode layer **202a** and the electrode layer **202b**, it is preferable that the gate insulating layer **104** have a stacked-layer structure including a nitride insulating layer **104a** and an oxide insulating layer **104b** and that the oxide insulating layer **104b** be in contact with the oxide semiconductor layer **316a**. The nitride insulating layer **104a** included in the gate insulating layer **104** can be used as a barrier layer for preventing diffusion of the low-resistance material. The oxide insulating layer **104b** prevents diffusion of nitrogen from the nitride insulating layer **104a** to the oxide semiconductor layers **316a** and **316b** and functions as a supply source of oxygen for the oxide semiconductor layers **316a** and **316b**.

The structure of the oxide semiconductor layer **316a** included in the transistor **300** can be the same as that of the oxide semiconductor layer **306a** of the transistor **310**; therefore, the above description can be referred to. The structure of the oxide semiconductor layer **316b** can be the same as that of the oxide semiconductor layer **306b** of the transistor **310**; therefore, the above description can be referred to. Therefore, in the band structure in the thickness direction of the stacked-layer structure in the transistor **300**, which includes the gate insulating layer **104**, the oxide semiconductor layer **316a**, the oxide semiconductor layer **316b**, the metal oxide layer **108**, and the oxide insulating layer **112**, as shown in FIG. 21B, the oxide semiconductor layer **316a** serves as a well; thus, the channel region is formed in the oxide semiconductor layer **316a** in the transistor including the stacked-layer structure.

Note that the connection between the electrode layer **202b** and the electrode layer **110c** in the transistor **300** is formed in such a manner that a metal oxide film and an oxide semiconductor film are processed into an island shape, and an opening portion is formed in the gate insulating layer **104** to expose the electrode layer **202b**. After that, a conductive film to be the pair of electrode layers **110a** and **110b** and the electrode layer **110c** is formed and processed, whereby the electrode layer **202b** and the electrode layer **110c** can be connected to each other.

The structure described in this embodiment makes it possible to obtain a highly reliable transistor in which the impu-

urity concentration of an oxide semiconductor layer including the channel formation region is reduced. Furthermore, the channel is less likely to be influenced by the interface state in the structure, so that a reduction in on-state current due to the interface state is less likely to occur. Accordingly, the transistor can have high on-state current and small S-value. In addition, a change in electrical characteristics due to the interface state is less likely to occur in the transistor, whereby the transistor has high reliability.

Note that the structure and method described in this embodiment can be implemented by being combined as appropriate with any of the other structures methods described in the other embodiments.

(Embodiment 4)

In this embodiment, a structural example of a display panel as a semiconductor device of one embodiment of the present invention is described.

<Display Panel>

A display panel including a semiconductor device such as any of the above-described transistors is described below.

FIG. 18A is a top view of the display panel of one embodiment of the present invention. FIG. 18B is a circuit diagram illustrating a pixel circuit that can be used in the case where a liquid crystal element is used in a pixel in the display panel of one embodiment of the present invention. FIG. 18C is a circuit diagram illustrating a pixel circuit that can be used in the case where an organic EL element is used in a pixel in the display panel of one embodiment of the present invention.

As the transistor to be disposed in the pixel portion, the transistor described in Embodiment 1 or 3 can be used. Further, the transistor can easily be an n-channel transistor, and thus, part of a driver circuit that can be formed using an n-channel transistor in the driver circuit is formed over the same substrate as the transistor of the pixel portion. With the use of the transistor described in Embodiment 1 or 3 for the pixel portion or the driver circuit in this manner, a highly reliable display device can be provided.

FIG. 18A is an example of a block diagram of an active matrix display device. A pixel portion 701, a first scan line driver circuit 702, a second scan line driver circuit 703, and a signal line driver circuit 704 are formed over a substrate 700 of the display device. In the pixel portion 701, a plurality of signal lines extended from the signal line driver circuit 704 is arranged and a plurality of scan lines extended from the first scan line driver circuit 702 and the second scan line driver circuit 703 is arranged. Note that pixels each including a display element are provided in matrix in respective regions in each of which the scan line and the signal line intersect with each other. The substrate 700 of the display device is connected to a timing control circuit (also referred to as a controller or a controller IC) through a connection portion such as a flexible printed circuit (FPC).

In FIG. 18A, the first scan line driver circuit 702, the second scan line driver circuit 703, and the signal line driver circuit 704 are formed over the same substrate 700 as the pixel portion 701. Accordingly, the number of components that are provided outside, such as a driver circuit, can be reduced, so that a reduction in cost can be achieved. Furthermore, if the driver circuit is provided outside the substrate 700, wirings would need to be extended and the number of connections of wirings would be increased, but by providing the driver circuit over the substrate 700, the number of connections of the wirings can be reduced. Consequently, an improvement in reliability or yield can be achieved.

[Liquid Crystal Panel]

FIG. 18B illustrates an example of a circuit configuration of a pixel in a liquid crystal panel as one mode of the display

panel. Here, a pixel circuit which is applicable to a pixel of a VA liquid crystal display panel is illustrated.

This pixel circuit can be applied to a structure in which one pixel includes a plurality of pixel electrode layers. The pixel electrode layers are connected to different transistors, and the transistors can be driven with different gate signals. Accordingly, signals applied to individual pixel electrode layers in a multi-domain pixel can be controlled independently.

A gate wiring 712 of a transistor 716 and a gate wiring 713 of a transistor 717 are separated so that different gate signals can be supplied thereto. In contrast, a source or drain electrode layer 714 that functions as a data line is shared by the transistors 716 and 717. The transistor described in Embodiment 3 can be used as appropriate as each of the transistors 716 and 717. In the above manner, a highly reliable liquid crystal display panel can be provided.

The shapes of a first pixel electrode layer electrically connected to the transistor 716 and a second pixel electrode layer electrically connected to the transistor 717 are described. The first pixel electrode layer and the second pixel electrode layer are separated by a slit. The first pixel electrode layer has a V shape and the second pixel electrode layer is provided so as to surround the first pixel electrode layer.

A gate electrode of the transistor 716 is connected to the gate wiring 712, and a gate electrode of the transistor 717 is connected to the gate wiring 713. When different gate signals are supplied to the gate wiring 712 and the gate wiring 713, operation timings of the transistor 716 and the transistor 717 can be varied. As a result, alignment of liquid crystals can be controlled.

In addition, a storage capacitor may be formed using a capacitor wiring 710, a gate insulating layer functioning as a dielectric, and a capacitor electrode electrically connected to the first pixel electrode layer or the second pixel electrode layer.

The multi-domain pixel includes a first liquid crystal element 718 and a second liquid crystal element 719. The first liquid crystal element 718 includes the first pixel electrode layer, a counter electrode layer, and a liquid crystal layer therebetween. The second liquid crystal element 719 includes the second pixel electrode layer, a counter electrode layer, and a liquid crystal layer therebetween.

Note that a pixel circuit of one embodiment of the present invention is not limited to that shown in FIG. 18B. For example, a switch, a resistor, a capacitor, a transistor, a sensor, or a logic circuit may be added to the pixel illustrated in FIG. 18B.

[Organic EL Panel]

As another mode of the display panel, an example of a circuit configuration of a pixel of an organic EL panel is shown in FIG. 18C.

In an organic EL element, by application of voltage to a light-emitting element, electrons are injected from one of a pair of electrodes and holes are injected from the other of the pair of electrodes, into a layer containing a light-emitting organic compound; thus, current flows. Then, recombination of the electrons and holes makes the light-emitting organic compound to form an excited state and to emit light when it returns from the excited state to a ground state. Based on such a mechanism, such a light-emitting element is referred to as a current-excitation type light-emitting element.

FIG. 18C illustrates an applicable example of a pixel circuit. In this example, one pixel includes two n-channel transistors. Note that the metal oxide film of one embodiment of the present invention can be used for channel formation regions of the n-channel transistors. Furthermore, digital time grayscale driving can be employed for the pixel circuit.

The configuration of the applicable pixel circuit and operation of a pixel employing digital time grayscale driving will be described.

A pixel 720 includes a switching transistor 721, a driver transistor 722, a light-emitting element 724, and a capacitor 723. A gate electrode layer of the switching transistor 721 is connected to a scan line 726, a first electrode (one of a source electrode layer and a drain electrode layer) of the switching transistor 721 is connected to a signal line 725, and a second electrode (the other of the source electrode layer and the drain electrode layer) of the switching transistor 721 is connected to a gate electrode layer of the driver transistor 722. The gate electrode layer of the driver transistor 722 is connected to a power supply line 727 through the capacitor 723, a first electrode of the driver transistor 722 is connected to the power supply line 727, and a second electrode of the driver transistor 722 is connected to a first electrode (a pixel electrode) of the light-emitting element 724. A second electrode of the light-emitting element 724 corresponds to a common electrode 728. The common electrode 728 is electrically connected to a common potential line provided over the same substrate.

As the switching transistor 721 and the driver transistor 722, the transistor described in Embodiment 3 can be used as appropriate. In this manner, a highly reliable organic EL display panel can be provided.

The potential of the second electrode (the common electrode 728) of the light-emitting element 724 is set to be a low power supply potential. Note that the low power supply potential is lower than a high power supply potential supplied to the power supply line 727. For example, the low power supply potential can be GND, 0V, or the like. The high power supply potential and the low power supply potential are set to be higher than or equal to the forward threshold voltage of the light-emitting element 724, and the difference between the potentials is applied to the light-emitting element 724, whereby current is supplied to the light-emitting element 724, leading to light emission. The forward voltage of the light-emitting element 724 refers to a voltage at which a desired luminance is obtained, and includes at least forward threshold voltage.

Note that gate capacitance of the driver transistor 722 may be used as a substitute for the capacitor 723, so that the capacitor 723 can be omitted. The gate capacitance of the driver transistor 722 may be formed between the channel formation region and the gate electrode layer.

Next, a signal input to the driver transistor 722 is described. In the case of a voltage-input voltage driving method, a video signal for sufficiently turning on or off the driver transistor 722 is input to the driver transistor 722. In order that the driver transistor 722 is operated in a linear region, voltage higher than the voltage of the power supply line 727 is applied to the gate electrode layer of the driver transistor 722. Note that voltage higher than or equal to voltage which is the sum of power supply line voltage and the threshold voltage V_{th} of the driver transistor 722 is applied to the signal line 725.

In the case of performing analog grayscale driving, a voltage greater than or equal to a voltage which is the sum of the forward voltage of the light-emitting element 724 and the threshold voltage V_{th} of the driver transistor 722 is applied to the gate electrode layer of the driver transistor 722. A video signal by which the driver transistor 722 is operated in a saturation region is input, so that current is supplied to the light-emitting element 724. In order that the driver transistor 722 is operated in a saturation region, the potential of the power supply line 727 is set higher than the gate potential of the driver transistor 722. When an analog video signal is used,

it is possible to supply current to the light-emitting element 724 in accordance with the video signal and perform analog grayscale driving.

Note that the configuration of the pixel circuit is not limited to that shown in FIG. 18C. For example, a switch, a resistor, a capacitor, a sensor, a transistor, a logic circuit, or the like may be added to the pixel circuit illustrated in FIG. 18C.

In the case where the transistor described in Embodiment 1 or 3 is used for the circuit shown in FIGS. 18A to 18C, the source electrode layer is electrically connected to the low potential side and the drain electrode layer is electrically connected to the high potential side.

For example, in this specification and the like, a display element, a display device, which is a device including a display element, a light-emitting element, and a light-emitting device, which is a device including a light-emitting element, can employ various modes or can include various elements. Examples of a display element, a display device, a light-emitting element, or a light-emitting device include a display medium whose contrast, luminance, reflectance, transmittance, or the like is changed by electromagnetic action, such as an electroluminescence (EL) element (e.g. an EL element including organic and inorganic materials, an organic EL element, or an inorganic EL element), an LED (e.g., a white LED, a red LED, a green LED, or a blue LED), a transistor (a transistor that emits light depending on current), an electron emitter, a liquid crystal element, electronic ink, an electrophoretic element, a grating light valve (GLV), a plasma display panel (PDP), a micro electro mechanical system (MEMS), a digital micromirror device (DMD), a digital micro shutter (DMS), interferometric modulator display (IMOD) element, an electrowetting element, a piezoelectric ceramic display, or a carbon nanotube. Note that examples of display devices having EL elements include an EL display. Examples of display devices including electron emitters are a field emission display (FED) and an SED-type flat panel display (SED: surface-conduction electron-emitter display). Examples of display devices including liquid crystal elements include a liquid crystal display (e.g., a transmissive liquid crystal display, a transreflective liquid crystal display, a reflective liquid crystal display, a direct-view liquid crystal display, or a projection liquid crystal display). An example of a display device including electronic ink or electrophoretic elements is electronic paper.

This embodiment can be combined with any of the other embodiments disclosed in this specification as appropriate. (Embodiment 5)

In this embodiment, a display module and electronic appliances that can be formed using a semiconductor device of one embodiment of the present invention are described.

In a display module 8000 illustrated in FIG. 19, a touch panel 8004 connected to an FPC 8003, a display panel 8006 connected to an FPC 8005, a backlight unit 8007, a frame 8009, a printed board 8010, and a battery 8011 are provided between an upper cover 8001 and a lower cover 8002. Note that the backlight unit 8007, the battery 8011, the touch panel 8004, and the like are not provided in some cases.

The semiconductor device of one embodiment of the present invention can be used for, for example, the display panel 8006.

The shapes and sizes of the upper cover 8001 and the lower cover 8002 can be changed as appropriate in accordance with the sizes of the touch panel 8004 and the display panel 8006.

The touch panel 8004 can be a resistive touch panel or a capacitive touch panel and can be used overlapping with the display panel 8006. A counter substrate (sealing substrate) of the display panel 8006 can have a touch panel function. A

47

photosensor may be provided in each pixel of the display panel **8006** to form an optical touch panel. An electrode for a touch sensor may be provided in each pixel of the display panel **8006** so that a capacitive touch panel is obtained.

The backlight unit **8007** includes a light source **8008**. The light source **8008** may be provided at an end portion of the backlight unit **8007** and a light diffusing plate may be used.

The frame **8009** protects the display panel **8006** and functions as an electromagnetic shield for blocking electromagnetic waves generated by the operation of the printed board **8010**. The frame **8009** can function as a radiator plate.

The printed board **8010** is provided with a power supply circuit and a signal processing circuit for outputting a video signal and a clock signal. As a power source for supplying power to the power supply circuit, an external commercial power source or a power source using the battery **8011** provided separately may be used. The battery **8011** can be omitted in the case of using a commercial power source.

The display module **8000** may be additionally provided with a member such as a polarizing plate, a retardation plate, or a prism sheet.

FIGS. **20A** to **20D** are external views of electronic appliances each including the semiconductor device of one embodiment of the present invention.

Examples of electronic appliances are a television set (also referred to as a television or a television receiver), a monitor of a computer or the like, a camera such as a digital camera or a digital video camera, a digital photo frame, a mobile phone handset (also referred to as a mobile phone or a mobile phone device), a portable game machine, a portable information terminal, an audio reproducing device, a large-sized game machine such as a pachinko machine, and the like.

FIG. **20A** illustrates a portable information terminal including a main body **1001**, a housing **1002**, display portions **1003a** and **1003b**, and the like. The display portion **1003b** is a touch panel. By touching a keyboard button **1004** displayed on the display portion **1003b**, a screen can be operated, and text can be input. It is needless to say that the display portion **1003a** may be a touch panel. A liquid crystal panel or an organic light-emitting panel is fabricated using any of the transistors described in the above embodiments as a switching element and used in the display portion **1003a** or **1003b**, whereby a highly reliable portable information terminal can be provided.

The portable information terminal illustrated in FIG. **20A** can have a function of displaying various kinds of information (e.g., a still image, a moving image, and a text image); a function of displaying a calendar, the date, the time, and the like on the display portion; a function of operating or editing the information displayed on the display portion; a function of controlling processing by various kinds of software (programs); and the like. Furthermore, an external connection terminal (an earphone terminal, a USB terminal, or the like), a recording medium insertion portion, and the like may be provided on the back surface or the side surface of the housing.

The portable information terminal illustrated in FIG. **20A** may transmit and receive data wirelessly. Through wireless communication, desired book data or the like can be purchased and downloaded from an e-book server.

FIG. **20B** illustrates a portable music player including, in a main body **1021**, a display portion **1023**, a fixing portion **1022** with which the portable music player can be worn on the ear, a speaker, an operation button **1024**, an external memory slot **1025**, and the like. A liquid crystal panel or an organic light-emitting panel is fabricated using any of the transistors described in the above embodiments as a switching element

48

and used in the display portion **1023**, whereby a highly reliable portable music player can be provided.

Furthermore, when the portable music player illustrated in FIG. **20B** has an antenna, a microphone function, or a wireless communication function and is used with a mobile phone, a user can talk on the phone wirelessly in a hands-free way while driving a car or the like.

FIG. **20C** illustrates a mobile phone including two housings, a housing **1030** and a housing **1031**. The housing **1031** includes a display panel **1032**, a speaker **1033**, a microphone **1034**, a pointing device **1036**, a camera **1037**, an external connection terminal **1038**, and the like. The housing **1030** is provided with a solar cell **1040** for charging the mobile phone, an external memory slot **1041**, and the like. In addition, an antenna is incorporated in the housing **1031**. Any of the transistors described in the above embodiments is used in the display panel **1032**, whereby a highly reliable mobile phone can be provided.

Furthermore, the display panel **1032** includes a touch panel. A plurality of operation keys **1035** which are displayed as images are indicated by dotted lines in FIG. **20C**. Note that a boosting circuit by which a voltage output from the solar cell **1040** is increased to be sufficiently high for each circuit is also included.

In the display panel **1032**, the direction of display is changed as appropriate depending on the application mode. Furthermore, the mobile phone is provided with the camera **1037** on the same surface as the display panel **1032**, and thus it can be used as a video phone. The speaker **1033** and the microphone **1034** can be used for videophone calls, recording, and playing sound, etc. as well as voice calls. Moreover, the housings **1030** and **1031** in a state where they are developed as illustrated in FIG. **20C** can shift, by sliding, to a state where one overlaps with the other. Therefore, the size of the mobile phone can be reduced, which makes the mobile phone suitable for being carried around.

The external connection terminal **1038** can be connected to an AC adaptor and a variety of cables such as a USB cable, whereby charging and data communication with a personal computer or the like are possible. In addition, by inserting a recording medium into the external memory slot **1041**, a larger amount of data can be stored and moved.

In addition to the above functions, an infrared communication function, a television reception function, or the like may be provided.

FIG. **20D** illustrates an example of a television set. In a television set **1050**, a display portion **1053** is incorporated in a housing **1051**. Images can be displayed on the display portion **1053**. Moreover, a CPU is incorporated in a stand **1055** for supporting the housing **1051**. Any of the transistors described in the above embodiments is used in the display portion **1053** and the CPU, whereby the television set **1050** can be highly reliable.

The television set **1050** can be operated with an operation switch of the housing **1051** or a separate remote controller. Further, the remote controller may be provided with a display portion for displaying data output from the remote controller.

Note that the television set **1050** is provided with a receiver, a modem, and the like. With the use of the receiver, general television broadcasting can be received. Moreover, when the television set is connected to a communication network with or without wires via the modem, one-way (from a sender to a receiver) or two-way (between a sender and a receiver or between receivers) information communication can be performed.

Furthermore, the television set **1050** is provided with an external connection terminal **1054**, a storage medium record-

ing and reproducing portion **1052**, and an external memory slot. The external connection terminal **1054** can be connected to various types of cables such as a USB cable, and data communication with a personal computer or the like is possible. A disk storage medium is inserted into the storage medium recording and reproducing portion **1052**, and reading data stored in the storage medium and writing data to the storage medium can be performed. In addition, an image, a video, or the like stored as data in an external memory **1056** inserted into the external memory slot can be displayed on the display portion **1053**.

Further, in the case where the off-state leakage current of the transistor described in the above embodiments is extremely small, when the transistor is used in the external memory **1056** or the CPU, the television set **1050** can have high reliability and sufficiently reduced power consumption.

This embodiment can be combined with any of the other embodiments disclosed in this specification as appropriate.

Example 1

In this example, transistors of one embodiment of the present invention were formed and their initial characteristics were measured. Furthermore, a band diagram of an oxide semiconductor layer and a metal oxide layer included in each transistor was measured. In addition, diffusion of copper in the metal oxide layer included in each transistor was evaluated. Results thereof are described.

First, a method for forming the transistors used in this example is described below. In this example, transistors having a structure similar to that of the transistor **200** illustrated in FIGS. **1A** and **1B** were formed.
(Sample A1)

A method for forming Sample A1 is described.

A glass substrate was used as the substrate **100**, and a 150-nm-thick tungsten film was deposited as a conductive film over the substrate **100** by a sputtering method. Next, the conductive film was selectively processed using a mask formed by a photolithography method to form the gate electrode layer **102**.

Then, the gate insulating layer **104** was formed over the substrate **100** and the gate electrode layer **102**. Here, as the gate insulating layer **104**, a 400-nm-thick silicon nitride film and a 50-nm-thick silicon oxynitride film were deposited by a CVD method.

Next, as an oxide semiconductor film, a 35-nm-thick In—Ga—Zn oxide film (hereinafter also referred to as IGZO (1:1:1)) was deposited over the gate insulating layer **104** by a sputtering method using an oxide target having an atomic ratio of In:Ga:Zn=1:1:1. Deposition conditions were as follows: an atmosphere of argon and oxygen (argon:oxygen=20 sccm:10 sccm), a pressure of 0.4 Pa, a power (DC) of 200 kW, and a substrate temperature of 300° C.

After the oxide semiconductor film was formed, a metal oxide film was successively formed without exposure to the air. As the metal oxide film, a 20-nm-thick In—Ga oxide film (hereinafter also referred to as IGO (1:1)) was deposited by a sputtering method using an oxide target having an atomic ratio of In:Ga=7:93. Deposition conditions were as follows: an atmosphere of argon and oxygen (argon:oxygen=20 sccm:10 sccm), a pressure of 0.4 Pa, a power (DC) of 200 kW, and a substrate temperature of 300° C.

After the heat treatment, the oxide semiconductor film and the metal oxide film were processed into an island shape using a mask formed by a photolithography method to form the oxide semiconductor layer **106** and the metal oxide layer **108**.

Next, heat treatment was performed at 450° C. for one hour in a nitrogen atmosphere, and then heat treatment was performed at 450° C. for one hour in a mixed atmosphere containing oxygen and nitrogen in the same treatment chamber.

A 30-nm-thick tungsten film and a 200-nm-thick copper film were deposited as a conductive film over the oxide semiconductor layer **106** and metal oxide layer **108** which had island shapes.

Then, the tungsten film and the copper film were selectively etched using a mask formed by a photolithography method to form the pair of electrode layers **110a** and **110b**.

Next, a 50-nm-thick silicon oxynitride film was deposited as the oxide insulating layer **112** over the gate insulating layer **104**, the metal oxide layer **108**, and the pair of electrode layers **110a** and **110b** by a CVD method. Subsequently, a 400-nm-thick silicon oxynitride film was successively deposited as the oxide insulating layer **114** by a CVD method without exposure to the air.

After that, heat treatment was performed at 350° C. for one hour in a mixed atmosphere containing oxygen and nitrogen.

Next, a 100-nm-thick silicon nitride film was deposited as the nitride insulating layer **116** over the oxide insulating layer **114** by a CVD method.

Then, although not illustrated, part of each of the oxide insulating layer **112**, the oxide insulating layer **114**, and the nitride insulating layer **116** was etched using a mask formed by a photolithography method to form an opening portion where one of the pair of electrode layers **110a** and **110b** was exposed.

Subsequently, a 100-nm-thick indium oxide-tin oxide compound (ITO-SiO₂) film containing silicon oxide was formed as a conductive film over the nitride insulating layer **116** by a sputtering method. Then, part of the conductive film was etched using a mask formed by a photolithography method to form a conductive layer in contact with one of the pair of electrode layers **110a** and **110b**. After that, heat treatment was performed at 250° C. for one hour in a nitrogen atmosphere.

Next, a 1.6-μm-thick polyimide layer was formed as a planarization layer (not illustrated) over the nitride insulating layer **116** and the conductive layer. Here, after a composition was applied to the nitride insulating layer **116**, light exposure and development were performed, and heat treatment was performed at 300° C. for one hour in an atmosphere containing nitrogen, whereby to form the planarization layer having an opening portion where part of the pair of electrode layers **110a** and **110b** was exposed.

Through the above process, Sample A1 was formed.

(Sample A2)

Sample A2, which is a comparative example, was formed under the same formation conditions as those of Sample A1 to have the same structure as Sample A1 except that the metal oxide layer **108** is not provided.

(Sample A3)

Sample A3, which is a comparative example, was formed under the same formation conditions as Sample A1 to have the same structure as Sample A1 except that an oxide semiconductor layer is provided instead of the metal oxide layer **108**. Specifically, a sample in which an oxide semiconductor film to be the oxide semiconductor layer was deposited under the following conditions was formed as Sample A3.

As the oxide semiconductor film, a 20-nm-thick In—Ga—Zn oxide film (hereinafter also referred to as IGZO(1:3:6)) was formed by a sputtering method using an oxide target with an atomic ratio of In:Ga:Zn=1:3:6. Deposition conditions were as follows: an atmosphere of argon and oxygen (argon:

oxygen=20 sccm:10 sccm), a pressure of 0.4 Pa, a power (DC) of 200 kW, and a substrate temperature of 200° C. (Sample A4)

Sample A4, which is a comparative example, was formed under the same formation conditions as Sample A1 to have the same structure as Sample A1 except that an oxide semiconductor layer is provided instead of the metal oxide layer 108. Specifically, a sample in which an oxide semiconductor film to be the oxide semiconductor layer was deposited under the following conditions was formed as Sample A4.

As the oxide semiconductor film, a 20-nm-thick In—Ga—Zn oxide film (also referred to as IGZO(1:6:4)) was formed by a sputtering method using an oxide target with an atomic ratio of In:Ga:Zn=1:6:4. Deposition conditions were as follows: an atmosphere of argon and oxygen (argon:oxygen=20 sccm:10 sccm), a pressure of 0.4 Pa, a power (DC) of 200 kW, and a substrate temperature of 200° C.

(Sample A5)

Sample A5, which is a comparative example, was formed under the same formation conditions as those of Sample A1 to have the same structure as Sample A1 except that a metal oxide layer in which the atomic ratio of indium to gallium is different from that in the metal oxide layer 108 is provided instead of the metal oxide layer 108. Specifically, a sample in which a metal oxide film to be the metal oxide layer was deposited under the following conditions was formed as Sample A5.

As the metal oxide layer, a 20-nm-thick In—Ga oxide film was deposited by a sputtering method using an oxide target having an atomic ratio of In:Ga=2:1 (such a metal oxide layer is also referred to as IGO(2:1)). Deposition conditions were as follows: an atmosphere of argon and oxygen (argon:oxygen=20 sccm:10 sccm), a pressure of 0.4 Pa, a power (DC) of 200 kW, and a substrate temperature of 300° C.

(Vg-Id Characteristics)

Next, Vg-Id characteristics of the transistors included in Sample A1 to Sample A5 were measured. Here, changes in characteristics of current flowing between a source electrode layer and a drain electrode layer (hereinafter referred to as drain current: Id), that is, Vg-Id characteristics were measured under the following conditions: the substrate temperature was 25° C., the potential difference between the source electrode layer and the drain electrode layer (hereinafter referred to as drain voltage: Vd) was 1 V or 10 V, and the potential difference between the source electrode layer and the gate electrode layer (hereinafter referred to as gate voltage: Vg) was changed from -20 V to 20 V. In each sample, the channel length L of the transistor was 6 μm and the channel width W thereof was 50 μm. Furthermore, each sample includes four transistors.

FIG. 11A shows Vg-Id characteristics of the transistors included in Sample A1. FIG. 12A shows Vg-Id characteristics of the transistors included in Sample A2. FIG. 13A shows Vg-Id characteristics of the transistors included in Sample A3. FIG. 14A shows Vg-Id characteristics of the transistors included in Sample A4. FIG. 15A shows Vg-Id characteristics of the transistors included in Sample A5. In each of FIG. 11A, FIG. 12A, FIG. 13A, FIG. 14A, and FIG. 15A, the horizontal axis represents gate voltage Vg, the first vertical axis represents drain current Id, and the second vertical axis represent field-effect mobility. Here, to show field-effect mobility in a saturation region, field-effect mobility calculated when Vd=10 V is shown.

FIG. 11A shows that the transistors of Sample A1 have high on-state current and excellent Vg-Id characteristics.

Meanwhile the Vg-Id characteristics in FIG. 12A reveal that on-state current is reduced in the transistors of Sample

A2. A possible cause of the reduction in on-state current is trapping of a conduction electron due to a shallow trap level in an oxide semiconductor layer. The shallow trap level is formed owing to Cu which has been included in the pair of electrode layers 110a and 110b and then moved to the surface of the oxide semiconductor layer 106 or into the oxide semiconductor layer 106.

The Vg-Id characteristics in FIG. 13A show that the threshold voltages of the transistors included in Sample A3 at a drain voltage of 1 V is different from those at a drain voltage of 10 V.

The Vg-Id characteristics in FIG. 14A show that the threshold voltages of the transistors included in Sample A4 at a drain voltage of 1 V is different from those at a drain voltage of 10 V. Furthermore, it is found from FIG. 14A that some of the transistors do not have switching characteristics.

The Vg-Id characteristics in FIG. 15A show that on-state current is reduced in the transistors included in Sample A5. (Band Diagram)

Next, measurement was performed using a spectroscopic ellipsometer to obtain a difference between the energy Ec of the bottom of the conduction band and the energy Ev of the top of the valence band, that is, the energy gap Eg of each of the following layers: the oxide semiconductor layers and the metal oxide layers of Samples A1 and A5, the oxide semiconductor layer of Sample A2, and the stacked oxide semiconductor layers of Samples A3 and A4. Furthermore, an energy difference between the vacuum level Evac and the valence band top Ev, i.e., the ionization potential Ip, was measured by ultraviolet photoelectron spectroscopy (UPS). Then, an energy difference between the vacuum level Evac and the bottom of the conduction band Ec, i.e., the electron affinity χ, was calculated by calculating a difference between the ionization potential Ip and the energy gap Eg, and a band diagram of each sample was obtained.

FIG. 11B shows a band diagram of Sample A1. FIG. 12B shows a band diagram of Sample A2. FIG. 13B shows a band diagram of Sample A3. FIG. 14B shows a band diagram of Sample A4. FIG. 15B shows a band diagram of Sample A5.

As shown in FIG. 11B, a difference in electron affinity χ between the oxide semiconductor layer (IGZO(1:1:1)) and the metal oxide layer (IGO(7:92)) is as large as 0.5 eV. Furthermore, as shown in FIG. 14B, a difference in electron affinity χ between the stacked oxide semiconductor layers (IGZO(1:1:1) and IGZO(1:6:4)) is as large as 0.5 eV.

Meanwhile, as shown in FIG. 13B, a difference in electron affinity χ between the stacked oxide semiconductor layers (IGZO(1:1:1) and IGZO(1:3:6)) is as small as 0.2 eV in Sample A3. Furthermore, as shown in FIG. 15B, difference in electron affinity χ between the oxide semiconductor layer (IGZO(1:1:1)) and the metal oxide layer (IGO(2:1)) is as small as 0.2 eV in Sample A5.

These results indicate that, as shown in the case of Sample A1, when such a metal oxide layer as shown in Embodiment 1 is used as the metal oxide layer provided between the oxide semiconductor layer and the pair of electrode layers, a band offset of the bottom of the conduction band Ec can be formed between the oxide semiconductor layer and the metal oxide layer.

Meanwhile, as shown in the case of Sample A3, when an energy difference in the bottom of the conduction band Ec between the stacked oxide semiconductor layers is small, a band offset of the bottom of the conduction band Ec is less likely to be formed between the oxide semiconductor layer (IGZO(1:1:1)) and the oxide semiconductor layer (IGZO(1:6:4)), and thus carriers also flow in the oxide semiconductor layer (IGZO(1:6:4)).

(Analysis on Cu Concentration by SIMS)

Then, diffusion of Cu in the metal oxide layer or the oxide semiconductor layer in contact with the pair of electrode layers 110a and 110b in each of Sample A1 and Samples A3 to A5 was analyzed by measurement of Cu concentration.

Here, a stack including a metal oxide film and a copper film was formed on a substrate to form a sample. First of all, a process for manufacturing each samples is described.

(Sample A6)

Sample A6 was formed as follows. A 100-nm-thick In—Ga oxide film (IGO(7:93)) was deposited as a metal oxide film on a glass substrate.

Next, a 60-nm-thick copper film was deposited on the metal oxide film. After that, a 100-nm-thick silicon nitride film was deposited on the copper film, and then heat treatment was performed at 350° C. for one hour in a mixed atmosphere containing nitrogen and oxygen.

Note that the metal oxide film (IGO(7:93)) was formed under the same conditions as the metal oxide film (IGO(7:93)) of Sample A1.

Through the above process, Sample A6 was formed.

(Sample A7)

Sample A7 was formed under the same formation conditions as Sample A6 to have the same structure as Sample A6 except that an oxide semiconductor film (IGZO(1:3:6)) was provided instead of the metal oxide film. Note that the oxide semiconductor film (IGZO(1:3:6)) was formed under the same conditions as the oxide semiconductor film (IGZO(1:3:6)) in Sample A3.

(Sample A8)

Sample A8 was formed under the same formation conditions as Sample A6 to have the same structure as Sample A6 except that an oxide semiconductor film (IGZO(1:6:4)) was provided instead of the metal oxide film. Note that the oxide semiconductor film (IGZO(1:6:4)) was formed under the same conditions as the oxide semiconductor film (IGZO(1:6:4)) in Sample A4.

(Sample A9)

Sample A9 was formed under the same formation conditions as Sample A6 to have the same structure as Sample A6 except that a metal oxide film (IGO(2:1)) in which the atomic ratio of indium to gallium is different from that in the metal oxide layer included in Sample A6 is provided instead of the metal oxide film. Note that the metal oxide film (IGO(2:1)) was deposited under the same conditions as the metal oxide film (IGO(2:1)) of Sample A5.

Next, the Cu concentration of each of Samples A6 to A9 was measured. The Cu concentration was measured using secondary ion mass spectrometry (SIMS). Note that the measurement of the Cu concentration was performed from the substrate side.

FIG. 11C shows analysis results of the Cu concentration of Sample A6. FIG. 13C shows analysis results of the Cu concentration of Sample A7. FIG. 14C shows analysis results of the Cu concentration of Sample A8. FIG. 15C shows analysis results of the Cu concentration of Sample A9.

Here, in a channel region of the transistor, the Cu concentration which affects the electrical characteristics is higher than or equal to 1×10^{18} atoms/cm³.

As shown in FIG. 11C, a region having a Cu concentration of 1×10^{18} atoms/cm³ in Sample A6 is a region which is closer to the substrate than the interface between the copper film and the metal oxide film (IGO(7:93)) by approximately 10 nm.

As shown in FIG. 13C, a region having a Cu concentration of 1×10^{18} atoms/cm³ in Sample A7 is a region which is closer

to the substrate than the interface between the copper film and the oxide semiconductor film (IGZO(1:3:6)) by approximately 10 nm.

Meanwhile, as shown in FIG. 14C, a region having a Cu concentration of 1×10^{18} atoms/cm³ in Sample A8 is closer to the substrate than the interface between the copper film and the oxide semiconductor film (IGZO(1:6:4)) by approximately 16 nm.

Furthermore, as shown in FIG. 15C, a region having a Cu concentration of 1×10^{18} atoms/cm³ in Sample A9 is closer to the substrate than the interface between the copper film and the metal oxide film (IGO(2:1)) by approximately 15 nm.

Comparison between Sample A6 and Sample A9 reveals that the diffusion length of copper (Cu) can be small in the metal oxide film in which the atomic ratio of Ga to In is high.

Comparison between Sample A7 and Sample A8 reveals that the diffusion length of copper (Cu) can be small in the oxide semiconductor film in which the atomic ratio of Zn to Ga is high. This is because when the atomic ratio of Zn to Ga is high, the proportion of a spinel crystal structure can be reduced.

According to the above results, the metal oxide layer which tends to form a band offset when it is in contact with the oxide semiconductor layer, and is capable of reducing the diffusion length of copper (Cu) is provided between the oxide semiconductor layer and the pair of electrode layers, whereby a transistor with high on-state current and excellent Vg-Id characteristics can be obtained.

Example 2

In this example, the crystal structure of a metal oxide film, the number of particles during deposition of the metal oxide film, and the band diagram of the metal oxide film were measured. The results are described.

(Method for Forming Samples)

In this example, samples were each formed in such a manner that a 100-nm-thick In—Ga oxide film was deposited as a metal oxide film on a quartz substrate.

Note that the samples were each formed using an oxide target having an atomic ratio of In:Ga=22:78, an oxide target having an atomic ratio of In:Ga=7:93, or an oxide target having an atomic ratio of In:Ga=2:98. Note that in the cases of using the oxide target having an atomic ratio of In:Ga=22:78 and the oxide target having an atomic ratio of In:Ga=7:93, a power (DC) of 200 kW was used. In the case of using the oxide target having an atomic ratio of In:Ga=2:98, a power (RF) of 400 kW was used.

Furthermore, a deposition atmosphere condition where the flow rate ratio of argon to oxygen was 20 sccm:10 sccm, or a deposition atmosphere condition where the flow rate of oxygen was 30 sccm was used.

In addition, a substrate temperature was 200° C. or 300° C.

Note that in each condition of the samples, the pressure in a chamber was 0.4 Pa.

(XRD Measurement)

Here, each sample was formed in such a manner that the substrate temperature was set to 300° C. and the metal oxide film was deposited using the oxide target. Then, the crystal structure of the metal oxide film of each sample was measured by XRD. The XRD measurement results are shown in FIG. 16.

According to FIG. 16, the metal oxide films formed using the oxide target having an atomic ratio of In:Ga=22:78 and the oxide target having an atomic ratio of In:Ga=7:93 have low crystallinity.

Meanwhile, a peak indicating a Ga_2O_3 crystal was observed in the metal oxide film which was formed using the oxide target having an atomic ratio of $\text{In}:\text{Ga}=2:98$ under the deposition atmosphere condition where the flow rate of oxygen was 30 sccm. Thus, these results show that a Ga_2O_3 crystal is included in the metal oxide film which is deposited in an oxygen atmosphere and in which the atomic ratio of Ga to In is high.

(Number of Particles in Deposition)

Next, analysis results of the relationship between the atomic ratio of metals contained in an oxide target and the number of generated particles are described.

A glass substrate was used instead of the quartz substrate in each sample used for the measurement. Furthermore, the metal oxide film was deposited using the oxide target under the deposition atmosphere conditions where the flow rate ratio of argon to oxygen was 20 sccm:10 sccm and the substrate temperature was 300° C.

Next, the number of particles on the glass substrate was measured before and after deposition of the metal oxide film with a test device using a laser. The results are shown in Table 1.

TABLE 1

Particle	IGO(In:Ga = 22:78)		IGO (In:Ga = 7:93)		IGO (In:Ga = 2:98)	
diameter (μm)	before deposition	after deposition	before deposition	after deposition	before deposition	after deposition
1.0-2.9	3	384	4	10	2	7
3.0-4.9	0	6	1	1	0	1
5.0-	0	0	1	2	0	0

Table 1 shows that the number of particles can be small after deposition by depositing the metal oxide film using the oxide target in which $y/(x+y)$ was greater than or equal to 0.9 where the atomic ratio of In to Ga was represented as $\text{In}:\text{Ga}=x:y$. According to the results, a transistor can be manufactured with high yield by depositing a metal oxide film using a target in which $y/(x+y)$ is greater than or equal to 0.9 where the atomic ratio of In to Ga is $\text{In}:\text{Ga}=x:y$.

(Band Diagram)

Next, in a manner similar to that of Example 1, energy gap E_g , ionization potential I_p , and electron affinity χ were obtained using a spectroscopic ellipsometer and an ultraviolet photoelectron spectroscopy, and a band diagram of each metal oxide film was obtained.

Note that the metal oxide film in each sample used for the measurement was deposited using the oxide target under the deposition atmosphere condition where the flow rate ratio of argon to oxygen was 20 sccm:10 sccm at a substrate temperature of 300° C.

FIG. 17 shows each band diagram of a metal oxide film (IGO(1:1)) deposited using an oxide target having an atomic ratio of $\text{In}:\text{Ga}=1:1$, a metal oxide film (IGO(22:78)) deposited using an oxide target having an atomic ratio of $\text{In}:\text{Ga}=22:78$, a metal oxide film (IGO(7:93)) deposited using an oxide target having an atomic ratio of $\text{In}:\text{Ga}=7:93$, and a metal oxide film (IGO(2:98)) deposited using an oxide target having an atomic ratio of $\text{In}:\text{Ga}=2:98$. Furthermore, as a reference example, a band diagram of an oxide semiconductor film (IGZO(1:1:1)) deposited using an oxide target having an atomic ratio of $\text{In}:\text{Ga}:\text{Zn}=1:1:1$ is shown.

As shown in FIG. 17, as the atomic ratio of Ga with respect to In in the oxide target becomes larger, a difference in the

electron affinity χ between the oxide semiconductor film and the metal oxide film is increased.

According to these results, the metal oxide layer as described in Embodiment 1, typically, a metal oxide layer in which $y/(x+y)$ is greater than or equal to 0.75 and less than 1, preferably greater than or equal to 0.78 and less than 1, further preferably greater than or equal to 0.80 and less than 1 where the atomic ratio of In to Ga is $\text{In}:\text{Ga}=x:y$ is used as the metal oxide layer provided between the oxide semiconductor layer and the pair of electrode layers, whereby a band offset of the bottom of the conduction band E_c can be formed between the oxide semiconductor layer and the metal oxide layer.

This application is based on Japanese Patent Application serial no. 2013-196333 filed with Japan Patent Office on Sep. 23, 2013, the entire contents of which are hereby incorporated by reference.

What is claimed is:

1. A semiconductor device comprising:

an oxide semiconductor layer;

a metal oxide layer comprising an In-M oxide in contact with the oxide semiconductor layer; and

a conductive layer in contact with the metal oxide layer, wherein the conductive layer comprises one of Cu, Al, Au, and Ag,

wherein the In-M oxide does not comprise Zn,

wherein M is one of Ti, Ga, Y, Zr, La, Ce, Nd, and Hf, and wherein $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where an atomic ratio of In to M included in the metal oxide layer is $\text{In}:\text{M}=x:y$.

2. The semiconductor device according to claim 1,

wherein the oxide semiconductor layer comprises a channel formation region, and wherein the conductive layer serves as a source electrode or a drain electrode.

3. The semiconductor device according to claim 1,

wherein M is Ga, and

wherein an element other than In, Ga and O is contained in the metal oxide layer at a concentration of less than or equal to 0.1%.

4. The semiconductor device according to claim 1,

wherein the conductive layer includes a first layer in contact with the metal oxide layer and a second layer in contact with the first layer,

wherein the first layer comprises one of Ti, Ta, Mo, and W, and

wherein the second layer comprises the one of Cu, Al, Au, and Ag.

5. The semiconductor device according to claim 1,

wherein the oxide semiconductor layer includes a first oxide semiconductor layer and a second oxide semiconductor layer between the first oxide semiconductor layer and the metal oxide layer, and

wherein a thickness of the first oxide semiconductor layer is larger than a thickness of the second oxide semiconductor layer.

6. The semiconductor device according to claim 5,

wherein electron affinity of the second oxide semiconductor layer is smaller than electron affinity of the first oxide semiconductor layer and larger than electron affinity of the metal oxide layer.

7. An electronic device comprising the semiconductor device according to claim 1.

8. A semiconductor device comprising:

a gate electrode layer;

a gate insulating layer over the gate electrode layer;

an oxide semiconductor layer over the gate electrode layer with the gate insulating layer therebetween;

57

a metal oxide layer comprising an In-M oxide over and in contact with the oxide semiconductor layer; and
 a pair of electrode layers in contact with the metal oxide layer,
 wherein the pair of electrode layers comprises one of Cu, Al, Au, and Ag,
 wherein the In-M oxide does not comprise Zn,
 wherein M is one of Ti, Ga, Y, Zr, La, Ce, Nd, and Hf, and
 wherein $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where an atomic ratio of In to M included in the metal oxide layer is In:M=x:y.

9. The semiconductor device according to claim 8,
 wherein M is Ga, and
 wherein an element other than In, Ga and O is contained in the metal oxide layer at a concentration of less than or equal to 0.1%.

10. The semiconductor device according to claim 8,
 wherein the pair of electrode layers includes a first layer in contact with the metal oxide layer and a second layer in contact with the first layer,
 wherein the first layer comprises one of Ti, Ta, Mo, and W, and
 wherein the second layer comprises the one of Cu, Al, Au, and Ag.

11. The semiconductor device according to claim 8,
 wherein the oxide semiconductor layer includes a first oxide semiconductor layer and a second oxide semiconductor layer between the first oxide semiconductor layer and the metal oxide layer, and
 wherein a thickness of the first oxide semiconductor layer is larger than a thickness of the second oxide semiconductor layer.

12. The semiconductor device according to claim 11,
 wherein electron affinity of the second oxide semiconductor layer is smaller than electron affinity of the first oxide semiconductor layer and larger than electron affinity of the metal oxide layer.

13. An electronic device comprising the semiconductor device according to claim 8.

14. A semiconductor device comprising:
 a first gate electrode layer;
 a first gate insulating layer over the first gate electrode layer;
 an oxide semiconductor layer over the first gate electrode layer with the first gate insulating layer therebetween;
 a metal oxide layer comprising an In-M oxide over and in contact with the oxide semiconductor layer;
 a pair of electrode layers in contact with the metal oxide layer;

58

a second gate insulating layer over and in contact with the pair of electrode layers; and
 a second gate electrode layer over the oxide semiconductor layer with the second gate insulating layer therebetween,
 wherein the pair of electrode layers comprises one of Cu, Al, Au, and Ag,
 wherein the In-M oxide does not comprise Zn,
 wherein M is one of Ti, Ga, Y, Zr, La, Ce, Nd, and Hf, and
 wherein $y/(x+y)$ is greater than or equal to 0.75 and less than 1 where an atomic ratio of In to M included in the metal oxide layer is In:M=x:y, and
 wherein the first gate electrode layer and the second gate electrode layer are electrically connected to each other through an opening in the first gate insulating layer and the second gate insulating layer.

15. The semiconductor device according to claim 14,
 wherein M is Ga, and
 wherein an element other than In, Ga and O is contained in the metal oxide layer at a concentration of less than or equal to 0.1%.

16. The semiconductor device according to claim 14,
 wherein the pair of electrode layers includes a first layer in contact with the metal oxide layer and a second layer in contact with the first layer,
 wherein the first layer comprises one of Ti, Ta, Mo, and W, and
 wherein the second layer comprises the one of Cu, Al, Au, and Ag.

17. The semiconductor device according to claim 14,
 wherein the oxide semiconductor layer includes a first oxide semiconductor layer and a second oxide semiconductor layer between the first oxide semiconductor layer and the metal oxide layer, and
 wherein a thickness of the first oxide semiconductor layer is larger than a thickness of the second oxide semiconductor layer.

18. The semiconductor device according to claim 17,
 wherein electron affinity of the second oxide semiconductor layer is smaller than electron affinity of the first oxide semiconductor layer and larger than electron affinity of the metal oxide layer.

19. The semiconductor device according to claim 14,
 wherein side surfaces of the oxide semiconductor layer face the second gate electrode layer with the second gate insulating layer therebetween.

20. An electronic device comprising the semiconductor device according to claim 14.

* * * * *